Applied Catalysis B: Environmental 103 (2011) 275–286

Contents lists available at ScienceDirect

Applied Catalysis B: Environmental

journal homepage: www.elsevier.com/locate/apcatb

Catalytic oxidation of toluene over binary mixtures of copper, manganese and cerium oxides supported on γ-Al_2O_3

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ARTICLE INFO

Article history:
Received 3 June 2010
Received in revised form
21 December 2010
Accepted 3 January 2011
Available online 8 January 2011

Keywords:
Toluene
VOC
Metal oxide
Manganese oxide
Copper oxide
Cerium oxide
Total oxidation
TPR
TPD
TPO

ABSTRACT

The catalytic oxidation of toluene has been investigated over binary mixtures of copper, manganese and cerium oxides supported on high surface area γ-Al_2O_3 in comparison with the corresponding single metal oxide components. Catalysts were synthesized with the impregnation method and were characterized with respect to their specific surface area (BET method), phase composition and mean crystallite size (XRD technique), reducibility (H_2-TPR) and adsorption/desorption characteristics toward toluene (TPD followed by TPO). Results obtained using a feed composition consisting of 1000 ppm toluene in air showed that the catalytic performance of mixed oxide catalysts can be improved significantly by proper selection of metal oxide (M_xO_y) loading and composition. The intrinsic activity of optimized catalysts, measured under differential reaction conditions, was found to be significantly higher compared to that of their single-component counterparts. This has been attributed to the better dispersion of the active M_xO_y phases, their increased reducibility (reactivity of surface oxygen), and their lower tendency to form coke deposits under reaction conditions. Addition of a second VOC (propane) or water vapor in the feed affected differently the activity of optimized-mixed oxide catalysts. As a general trend, inhibition by the presence of propane was more pronounced for CeO_2-containing samples whereas the presence of H_2O affected mainly the CuO_x-containing catalysts. It is concluded that the VOC oxidation activity of Al_2O_3-supported mixed oxide catalysts is determined by the reducibility of the dispersed active phases, which may be controlled by proper selection of M_xO_y nature, loading and composition.

1. Introduction

Volatile organic compounds (VOCs) are important air pollutants due to their toxic nature and their contribution to major environmental problems such as photochemical ozone formation, global warming and stratospheric ozone depletion [1]. Among the various conventional methods (e.g., incineration, condensation, adsorption, and absorption) and emerging technologies (e.g., treatment with spark-generated aerosol particles, negative air ions, electrical discharge, photooxidation, etc.) which have been proposed for the control of VOC emissions [2,3], catalytic oxidation is probably the most effective method for destructive removal of low concentrations of VOCs in large volumes of air [2,4,5], and may satisfy the increasingly stringent environmental regulations.

Two groups of catalytic materials are usually employed for "deep" (complete) oxidation of VOCs in air streams: (i) supported or unsupported noble metal catalysts (mainly Pt and Pd), and (ii) transition metal oxide-based catalysts. Noble metal catalysts are characterized by good stability and high activity at relatively low temperatures [2,4–7], but their high cost, their sensitivity to poisoning by chlorine and the formation of toxic polychlorinated compounds when used for total oxidation of chlorinated VOCs [8,9] have motivated the search for alternative catalysts. Transition metal oxide-based catalysts are less costly than noble metal catalysts, generally more resistant to poisoning and, in certain cases, they exhibit activity comparable to that of Pt/Al_2O_3 catalyst [10–14]. In addition, they usually possess higher metal content and, concomitantly, may have a substantially higher active surface area. Therefore, transition metal oxides have been explored intensively during the past years as effective and more economical catalysts for the total oxidation of VOCs.

A variety of metal oxide catalyst formulations have been evaluated for the deep oxidation of VOCs, including CuO_x [13–20], MnO_x [11,14–18,20–27], CeO_x [12,16,19,20,25,28], NiO_x [16–18], CoO_x [12,15,17,18,29,30], MoO_x [16–18,22], ZrO_x [16,20,22,28], CrO_x [18,20,22], VO_x [17,20,22], FeO_x [15,17,18], and their binary mixtures [12–14,18,19,25,26,28,31–38]. The activity of these materials for complete oxidation of VOCs has been found to depend on the nature and morphology of the support [15,18,22,24,27,30,36] and on the type of VOC investigated [14,15,18,21]. These dependences have been explained by considering that different active sites may be involved in the oxidation of different VOCs and that

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doi:10.1016/j.apcatb.2011.01.001

the reaction can be affected appreciably by electronic and geometric effects between the catalyst components [14]. It is generally believed that oxidation of hydrocarbons takes place via a redox mechanism in which the rate determining step is oxygen removal from the metal oxide [24,39,40]. Thus, the reducibility of metal oxide species appears to be one of the most critical parameters that affect catalytic performance for VOC oxidation [24,27]. Reducibility of a metal oxide, and therefore catalytic activity, can be improved in the presence of a second component, i.e., by using binary metal oxide catalysts [12–14,18,19,25,26,28,31–38].

In our previous study [20] we have investigated oxidation of toluene over supported Pt catalysts as well as over a variety of metal oxide (M_xO_y) catalysts dispersed on high-surface area γ-Al_2O_3. Toluene was chosen as a representative aromatic VOC because of its hazardous nature and of its presence in various sources such as printing, pressing, petrochemical industries, etc. Results obtained over M_xO_y/Al_2O_3 catalysts (M = Cu, Mn, Ce, V, Mg, Zr, Cr, Nd, Cs) showed that supported metal oxides exhibit relatively high activity, which seems to correlate well with the reducibility of dispersed M_xO_y phases [20]. It was also shown that catalytic performance can be optimized by proper selection of M_xO_y loading. Among the materials investigated, optimal results were obtained over 60% MnO_x, 70–90% CeO_2 and 5–10% CuO_x supported on Al_2O_3 [20].

In the present work, we investigate the catalytic performance of binary mixtures of Mn-, Ce- and Cu-oxides supported on high surface γ-Al_2O_3 in an attempt to develop more efficient catalyst formulations for toluene combustion. The catalytic performance of these materials was compared to that of the corresponding single oxide catalysts in order to investigate the correlation between physicochemical characteristics and reactivity of optimized materials.

2. Experimental

2.1. Catalyst preparation and characterization

Alumina-supported metal oxide catalysts of variable loading and composition were prepared by impregnation of high surface γ-Al_2O_3 powder (184 $m^2\,g^{-1}$, Engelhard) in an aqueous solution containing known amounts of $Cu(NO_3)_2{\cdot}3H_2O$, $Mn(NO_3)_2{\cdot}xH_2O$ and/or $Ce(NO_3)_3{\cdot}6H_2O$, following a procedure that has been described elsewhere [20,41]. The impregnated support was heated under continuous stirring at 70 °C to evaporate water, dried at 110 °C for 24 h and finally calcined in air at 450 °C for 2 h. Materials thus prepared are denoted in the following based on the wt.% loading of deposited M_xO_y species only, not including alumina. For instance, 10CuO–60MnO refers to a catalyst consisting of 10% CuO, 60% MnO and 30% Al_2O_3 (by weight).

The specific surface area (SSA) of synthesized materials was determined employing nitrogen physisorption at the temperature of liquid nitrogen with the use of a Quantachrome Corporation, 440-C BET apparatus. X-ray diffraction (XRD) patterns were obtained on a Pruker D8 advance powder diffractometer. Scans were collected in the range of 2θ between 20 and 80° with a scanning rate of 0.03°/s. The primary crystallite size of M_xO_y ($d_{M_xO_y}$) was calculated from X-ray line broadening by means of Scherrer's equation. Details of the apparatus and procedures used can be found elsewhere [20,42].

2.2. Temperature-programmed (TPD, TPO, TPR) experiments

Temperature-programmed reduction (TPR), desorption (TPD) and oxidation (TPO) experiments were carried out using the apparatus and following the procedures that have been described in detail elsewhere [20,43,44]. In a typical TPD experiment, an amount of catalyst (30 mg) in powder form was placed in a quartz microreactor and preoxidized at 300 °C with a flowing 3% O_2/He mixture for 30 min. The sample was then heated under He flow at 500 °C for 15 min to remove adsorbed species from the catalyst surface, and subsequently cooled down to room temperature. The flow was then switched to 0.2% C_7H_8/He for 30 min followed by purging with He for 30 min to remove weakly adsorbed toluene. Temperature programming was then initiated with a heating rate of $\beta = 30\,^{\circ}C\,min^{-1}$ and the TPD patterns of desorbed species were recorded with the use of a mass spectrometer (Omnistar, Pfeiffer Vacuum) connected on-line to the exit of the reactor.

TPO experiments were carried out immediately after TPD experiments, in order to estimate the amount of carbon-containing species deposited on the catalyst surface. For this, after completion of the TPD experiment, the sample was cooled down to room temperature under He flow. The feed was then switched to 3% O_2/He, left at 25 °C for 10 min and then heated linearly ($\beta = 30\,^{\circ}C\,min^{-1}$) to 750 °C.

Temperature-programmed reduction experiments were carried out over the preoxidized samples with the use of hydrogen as the reducing agent (H_2-TPR). The procedure used was similar to that described above for TPD experiments, with the exception that linear heating from 25 to 750 °C was done under a flow of 2% H_2/He mixture.

Calibration of the mass spectrometer was done with the use of self-prepared gas mixtures of accurately known composition. The flow rate in all temperature-programmed experiments reported here was 40 $cm^3\,min^{-1}$.

2.3. Catalytic performance tests and kinetic measurements

The catalytic performance of the synthesized materials for the oxidation of toluene was investigated in the temperature range of 150–450 °C. The apparatus used consists of a flow measuring and control system, the reactor and an on-line analysis system [20]. The flow system is equipped with four mass-flow controllers and two temperature-controlled saturators, which contain liquid phase toluene and water. The air streams which pass through the saturators are mixed with another air stream to give the desired feed composition. The catalyst, in powder form, is placed in the quartz reactor (7.0 mm i.d.) and held in place by means of quartz wool. Temperature is measured in the middle of the catalyst bed by means of a K-type thermocouple. All gas lines are heated constantly at 80 °C in order to minimize adsorption of toluene and water on tube walls. The analysis system consists of a gas chromatograph (Varian CP-3800) equipped with two columns (molecular sieve 5A and silicate 5CB) and two detectors (TCD and FID) and operates with He as the carrier gas. Determination of the response factors of the detectors was achieved with the use of gas streams of known composition (Scott specialty gas mixtures).

In a typical experiment, an amount of catalyst (usually 60 mg, with particle size of $0.18 < d_p < 0.25$ mm) was placed in the reactor, heated at 300 °C under He flow for 30 min and then calcined at 450 °C under air flow for 30 min. The sample was then conditioned at the same temperature for 30 min by exposure to the reaction mixture consisting of 1000 ppm toluene in air. Concentrations of reactants and products were then determined at steady-state conditions using the analysis system described above. Similar measurements were obtained following a stepwise decrease of temperature, until conversion of toluene dropped close to zero. Selected measurements were repeated by subsequent increase of temperature to check for possible catalyst deactivation. In all cases, data points presented here are averages of at least three measurements. The total flow rate was 200 $cm^3\,min^{-1}$ ($W/F = 0.018\,g\,s\,cm^{-3}$). Conversion of toluene (X_{tol}) was calculated based on inlet and outlet measured concentrations. It should be