The oxidation of trichloroethylene over different mixed oxides derived from hydrotalcites

Neus Blanch-Raga [a], A. Eduardo Palomares [a,*], Joaquín Martínez-Triguero [a], Marta Puche [a], Geolar Fetter [b], Pedro Bosch [c]

[a] Instituto de Tecnología Química, UPV-CSIC, Valencia 46022, Spain
[b] Facultad de Ciencias Químicas, BUAP, Puebla, PUE 72570, Mexico
[c] Instituto de Investigaciones en Materiales, UNAM, México D.F. 04510, Mexico

ARTICLE INFO

ABSTRACT

The activity of different Mg(Fe/Al), Ni(Fe/Al) and Co(Fe/Al) mixed oxides based on hydrotalcite-like compounds have been studied for the catalytic oxidation of trichloroethylene. It has been shown that the Co catalysts are more active than the Ni catalyst, being the Mg catalysts the less active ones. The activity of all the catalysts improves when iron is substituted by aluminum in the catalyst composition. The best results have been obtained with the CoAl mixed oxide derived from hydrotalcite that is a stable, highly active and selective catalyst. These results have been related with the presence of aluminum in the Co_3O_4 structure that favors, in the presence of oxygen, the formation of O_2^- sites and enhances the acid properties of the catalyst. The combination of both characteristics maximizes the adsorption and oxidation of the TCE.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Chlorinated volatile organic compounds (CVOCs) are widely used in industry in different processes as petrochemical manufacture and dry cleaning. They are recognized as important air pollutants and their emissions contribute to the ozone layer destruction, to the photochemical smog and to undesirable human health effects. Trichloroethylene (TCE) is a common CVOC pollutant that is toxic, stable and probably carcinogenic to humans [1]. To control CVOC's emissions from stationary sources, thermal incineration is the most commonly used process, but it has important energetic costs because it operates at temperatures higher than 700 °C and chlorinated by-products can be formed. An interesting option to control CVOC emissions is the catalytic oxidation that makes feasible the operation at lower temperatures (250–550 °C) [2–4]. Metal oxides [5–8] or supported noble metals [9–11]. have been the most common catalysts used in this reaction, but they have some drawbacks as the poisoning by chlorine [4] and the formation of chlorinated by-products that can be very toxic [7,12].

Recently, other materials have been used for the catalytic oxidation of CVOCs as zeolites [13,14] and bronzes [15], but it is still necessary to find more active and stable catalysts. An alternative could be the use of mixed oxides derived from hydrotalcite-like compounds as catalysts for the CVOC oxidation.

Hydrotalcites are two-dimensional layered synthetic materials with alternating positively charged mixed metal hydroxide sheets and negatively charged interlayer anions [16]. By changing the nature and the molar ratio of the metal cations as well as the type of interlayer anions, many isostructural materials with different physicochemical properties can be obtained. The calcination of hydrotalcites leads to the formation of mixed oxides with interesting properties for the CVOC's catalytic removal, such as small particle size, large specific area and homogeneous interdispersion of the metals [17–20]. This work studies the use of mixed oxides derived from hydrotalcites, containing transition metals with oxidative properties, for the TCE catalytic oxidation reaction. The catalysts prepared are different Mg(Fe/Al), Ni(Fe/Al) and Co(Fe/Al) oxides based on hydrotalcite-like compounds and their activity have been compared with that of a H-MOR zeolite, which is a conventional catalyst used for this reaction [21]. The catalysts have been characterized by different techniques, i.e. gas adsorption (S_{BET}), X-ray diffraction (XRD), temperature-programmed desorption (NH₃-TPD), temperature-programmed reduction (H₂-TPR) and elemental analysis through inductively coupled plasma (ICP), in

order to correlate their activity with the physical–chemical features of the materials.

2. Experimental

2.1. Catalysts preparation

The MgAl hydrotalcite was synthesized by mixing an aqueous solution (2.5 M) of $Mg(NO_3)_2 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ with a 1.86 M solution of NaOH to obtain the desired Mg/Al molar ratio at a constant pH of 9. The resulting gel was treated in a microwave autoclave (MIC-I, Sistemas y Equipos de Vidrio S.A. de C.V.) for 10 min operating at 2.45 GHz with a microwave irradiation power of 200 W, while the temperature was maintained at 80 °C. The solid was recovered by decantation and washed several times with distilled water until the residual solution reached a pH value of about 8. Finally, the solid was dried at 60 °C for 24 h and calcined in air at 550 °C for 6 h.

NiAl, CoAl, MgFe, NiFe, CoFe, MgFeAl, NiFeAl and CoFeAl hydrotalcites were synthesized by using the simultaneous co-precipitation technique. An aqueous solution with the appropriate amounts of $Ni(NO_3)_2 \cdot 6H_2O$, $Co(NO_3)_2 \cdot 6H_2O$ or $MgCl_2$ and $FeCl_3$ or $Al(NO_3)_3 \cdot 9H_2O$ was mixed with a NaOH and Na_2CO_3 solution. Both solutions were added simultaneously with a flow rate of 60 mL h^{-1} at room temperature and atmospheric pressure and they were mixed under vigorous stirring. The resulting gel was dried overnight at 60 °C. The product was then filtered off and washed thoroughly with distilled water. The dried hydrotalcite was calcined in air at 550 °C for 6 h.

Zeolite NH_4-MOR (CBV 10AH with $SiO_2/Al_2O_3 = 14$ and surface area of 490 m^2 g^{-1}) was supplied by Zeolyst Corp. and it was transformed into the H-form by calcination in air at 550 °C for 3 h.

2.2. Catalysts characterization

The chemical composition of the samples was measured by inductively coupled plasma (ICP-OES). Samples (*ca.* 20 mg), previously calcined, were dissolved in a HNO_3/HCl (1:3 vol.) solution and then analyzed in a Varian 715-ES ICP-Optical Emission Spectrometer.

BET surface areas were determined from the nitrogen adsorption–desorption curves by the conventional multipoint technique with a Micromeritics ASAP 2420. The samples were pretreated at 400 °C for 12 h at high vacuum.

A Phillips X'Pert diffractometer coupled to a copper anode X-ray tube was used for the XRD characterization, employing the K_α-Cu monochromatic radiation. Compounds were identified in the conventional way using the JCPDS file.

Temperature programmed reduction (TPR) experiments were carried out using a TPD-TPR Autochem 2910 analyzer equipped with a thermal conductivity detector (TCD). Samples (10–20 mg of catalyst) were treated with a N_2:H_2 flow (10% H_2) of 50 mL min^{-1} at a heating rate of 10 °C min^{-1} from room temperature to 800 °C.

Temperature programmed desorption of ammonia (TPD) experiments were carried out on a Micromeritics Autochem II analyzer, where 300 mg of sample were pre-treated in an Ar stream at 450 °C for 1 h. Ammonia was chemisorbed by pulses at 100 °C until equilibrium was reached. Then, the sample was fluxed with a He stream for 15 min, prior to increase the temperature up to 500 °C using a heating rate of 10 °C min^{-1}. The NH_3 desorption was monitored by both thermal conductivity detector (TCD) and mass-spectrometer, following the mass of ammonia at m/e = 15.

2.3. Catalysts activity

Catalytic oxidation reactions were carried out in a conventional quartz fixed bed reactor under atmospheric pressure. The catalysts were pelletized, and then crushed and sieved to obtain grains of 0.25–0.45 mm diameter. The catalyst bed (0.68 g) was supported on a quartz plug located into the reactor. Crushed quartz glass (>0.6 mm o.d.) was placed above the catalyst bed as a preheating zone of the incoming feed stream. The temperature was measured with a K-thermocouple located in the reactor, right before the catalyst bed. The reactor was housed in an electrically-heated furnace. Before reaction the calcined samples were activated at 150 °C with air during 30 min [15]. After activation, the gas mixture, composed by trichloroethylene (1000 ppm) and dry air, was introduced into the reactor at 400 mL min^{-1} (GHSV = 15,000 h^{-1}) and with a residence time of 0.24 s. The reaction was carried out under continuous flow of reactants, and each catalyst was tested at different temperatures, between 150 and 550 °C in steps of 50 °C keeping each temperature during 30 min. A blank experiment was made in the same reaction conditions but introducing only crushed quartz glass into the reactor without catalyst.

The reaction products (except Cl_2 and HCl) were separated, identified and quantified by a Bruker 450 gas chromatograph equipped with an HP-5 column. The concentration of TCE, as well as any other chlorinated hydrocarbon formed in the reaction was analyzed with a flame ionization detector, whilst the CO and CO_2 concentration was analyzed with a thermal conductivity detector. Analysis of both Cl_2 and HCl was performed by bubbling the effluent stream through a 0.125 M NaOH solution [22]. Cl_2 concentration was determined by titration with ferrous ammonium sulfate using *N,N*-diethyl-*p*-phenylenediamine as an indicator and the concentration of chloride ions in the solution was determined using an ion-selective electrode (Thermo Scientific, Orion Products).

3. Results and discussion

3.1. Catalysts characterization

Table 1 shows the specific surface area and the elemental composition of the calcined samples. The BET surface area of all samples varies between 80 and 255 m^2 g^{-1}, obtaining the highest values with the Mg-containing catalysts, and the lowest with the samples containing cobalt. This is related with the higher crystallite size of the cobalt catalysts compared with the magnesium catalysts [23] (*e.g.* the crystallite size calculated from the Debye–Scherrer equation is 12 nm for CoAl and 4 nm for MgAl). In all the samples the partial replacement of iron by aluminum results in an increase of the surface area because the presence of aluminum diminishes the mean crystallite size of the samples [23] (*e.g.* the crystallite size calculated from the Debye–Scherrer equation is 19 nm for CoFe and 14 nm for CoFeAl).

The XRD patterns of the samples before and after calcination are displayed in Figs. 1 and 2. Before calcination (Fig. 1), all the samples present the characteristic diffraction peaks of a typical nitrated hydrotalcite [24–26] around $2\theta = 10.9°$, $22.2°$, $34.2°$, $38.7°$, $44.7°$, $60.1°$ and $61.2°$, indicating that the hydrotalcite phase was successfully formed, independently of the preparation method and the nominal molar ratio. Nevertheless, the substitution of aluminum by iron in the hydrotalcite structure results in a modification of the peak broadening which can be attributed to a strain between the crystalline planes. Moreover the position of the peaks in the samples containing iron is shifted to lower values of 2θ degrees if compared with the samples with aluminum, due to the difference size of Fe^{3+} and Al^{3+} ions.