Chemosphere 64 (2006) 503–509

CHEMOSPHERE

www.elsevier.com/locate/chemosphere

Technical Note

Performance of the supported copper oxide catalysts for the catalytic incineration of aromatic hydrocarbons

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Received 28 June 2005; received in revised form 12 November 2005; accepted 16 November 2005

Abstract

A fixed bed reactor was used to assess the catalytic incineration of toluene by various transition-metal oxide species supported on γ-Al_2O_3. CuO/γ-Al_2O_3 was found to be the most active of seven catalysts investigated. The CuO species, with a Cu content of 5% (wt), was hence used with four different supports (CeO_2, γ-Al_2O_3, TiO_2 and V_2O_5) in order to define the optimal combination. Results of the catalytic incineration of toluene, X-ray diffraction (XRD) analysis, oxygen-temperature programmed desorption (O_2-TPD), toluene-temperature programmed desorption (toluene-TPD) and hydrogen-temperature programmed reduction (H_2-TPR) showed that CuO/CeO_2 was the most active catalyst, followed by CuO/γ-Al_2O_3. The activity of CuO/CeO_2 with respect to the VOC molecule was observed to follow this sequence: toluen > *p*-xylene > benzene. The addition of water vapor or CO_2 significantly inhibited the activity of the CuO/CeO_2 and CuO/γ-Al_2O_3 catalysts. The inhibiting effect of both was reversible for CuO/γ-Al_2O_3. For CuO/CeO_2, the inhibiting effect of CO_2 was reversible and even insignificant at a higher temperature (220 °C), but the effect of H_2O vapor was somewhat irreversible at lower incineration temperatures ($\leqslant$220 °C). For complete oxidation of toluene, the required reaction temperature increased with gas hourly space velocity (GHSV) and toluene inlet concentration.

Keywords: Catalytic incineration; Toluene; CuO/CeO_2; CuO/γ-Al_2O_3; TPD; TPR

1. Introduction

Volatile organic compounds (VOCs) are major contributors to air pollution. These VOCs, including alcohols, alkanes and aromatics, are easily vaporized at ambient temperature and pressure and may pollute the atmosphere directly or indirectly as secondary pollutants (Everaert and Baeyens, 2004). Their destruction is therefore necessary. Several techniques, e.g. adsorption, high-temperature incineration and catalytic incineration, have been developed for the abatement of VOCs, of which thermal and catalytic incineration is the most efficient. However, because the operating temperature of thermal incineration usually exceeds 750 °C, it is a somewhat cumbersome method, with the attendant disadvantages of high fuel cost, need for special construction materials, and possible production of undesirable by-products. Catalytic incineration requires temperatures in the range of 200–500 °C (Spivey, 1987) and is receiving an increased attention because of its energy saving potential (Van der Vaart et al., 1991a,b). Precious metals and base metal oxides are commonly used for the catalytic oxidation of VOCs. The noble metals platinum and palladium are recognized as the most typical species of precious metal catalysts (Baldwin and Burch, 1990; Garbowski et al., 1995; Lyubovski and Pfefferle, 1999), due to their higher activity and higher

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doi:10.1016/j.chemosphere.2005.11.023

resistance to sulfur poisoning (Farrauto and Bartholomew, 1997). The base metal oxides are usually prepared with a higher metal content and added at a higher catalyst loading, leading to an increased number of active sites in the metal oxide bed. This results in a catalyst that is only slightly less active than Pt/Al_2O_3 for the incineration of hydrocarbons. In fact, Heyes et al. (1982) found that CuO was equally as effective as Pt for the incineration of *n*-butanol and methyl mercaptan, with the order: $CuO = Pt > MnO_2 > V_2O_5 > Co_3O_4$, whilst Larsson and Andersson (2000) found excellent performance for the incineration of CO, ethyl acetate, and ethanol over CuO_x/Al_2O_3 and $CuO_x–CeO_2/Al_2O_3$, etc. Alternatively, Rajesh and Ozkan (1993) reported that CuO/Al_2O_3 was even more active than Pt/Al_2O_3 for the complete oxidation of ethanol. Moreover, Tseng and Chu (2001) reported excellent metal oxide catalyst activity (MnO/Fe_2O_3) in the catalytic oxidation of styrene and Spinicci et al. (2001) and Chang and Weng (1993) found another type of base metal catalyst, i.e. perovskite catalyst ($LaMO_3$, M = Mn, Co, Fe, Sr), was effective for the incineration of VOCs. Also note previous work of the author, using supported metal oxide as the catalyst, demonstrated that $CuO/\gamma\text{-}Al_2O_3$ was the most active catalyst for the catalytic incineration of dimethyl disulfide, whilst MoO_3 was the best promoter of $CuO/\gamma\text{-}Al_2O_3$ and Cr_2O_3 was the best promoter of the $CuO–MoO_3/\gamma\text{-}Al_2O_3$ catalyst (Wang and Weng, 1997, 1998a,b; Wang et al., 2002). Furthermore, for incinerating VOCs by metal oxide/$\gamma\text{-}Al_2O_3$, Wang (2004) has identified the most active metal species, i.e. CuO, and the optimum Cu content. Nevertheless, performance of supported CuO catalyst can be further improved, and using different support may be promising. As a result, the purpose of the present paper was to screen the most suitable combination of CuO and various supports for the catalytic incineration of toluene. Note that because toluene can be produced from diverse sources, e.g. from printing, pressing, and petrochemical industries and because it is narcotic in high concentrations and induces mild macrocytic anemia in those working with it, toluene is therefore a good representative of the VOC group, and was chosen to assess the feasibility of catalytic incineration of aromatics using a supported metal oxide catalyst.

In this work, firstly several transition-metal species supported on $\gamma\text{-}Al_2O_3$ were tested to find the most active one. Then, the most active species was impregnated onto various supports (CeO_2, $\gamma\text{-}Al_2O_3$, TiO_2, and V_2O_5) to find an optimal combination. The catalyst activity was evaluated using X-ray diffraction (XRD), BET surface area measurement, oxygen-temperature programmed desorption (O_2-TPD), toluene-temperature programmed desorption (toluene-TPD) and hydrogen-temperature programmed reduction (H_2-TPR). The investigation moreover included both the effect of adding water vapor or CO_2, and the effect of varying the gas hourly space velocity (GHSV) and toluene concentration.

2. Experimental

2.1. Catalyst preparation

The supports (CeO_2, $\gamma\text{-}Al_2O_3$, TiO_2 or V_2O_5, purchased from Merck Co.) were dried in a vacuum oven at 120 °C for 12 h and cooled to room temperature in a desiccator. A known amount of metal salt (Cu, Fe, Mn, Cr, Co, Mo or Ni) in deionized water (7 ml) was thereafter added. Supports and salts were of commercial grade. The well-impregnated catalyst supports were stirred for 0.5 h, dried in air at 120 °C for 24 h and, pulverized to particle sizes between 140 and 220 mesh (0.11–0.077 mm), calcined with air at 500 °C for 8 h. The metal loading was fixed at 5% for all catalysts.

2.2. Measurement of activity

The catalyst activity was assessed by conducting complete oxidation tests for toluene in a tubular reactor (1.27 cm o.d. Pyrex). In each run about 0.5 g of catalyst was used, mixed with 0.5 g of powdered quartz to disperse the catalyst. To prevent an over-estimation of VOC conversion caused by adsorption of VOC in the initial stages of the test, the catalyst was pretreated at 200 °C for 1.5 h under the test flows of reactant mixture (4000 ppm toluene balanced by dry air with 20.5% O_2) at GHSV of 4500 h^{-1}. The GHSV was thereafter varied between 4500 and 13 500 h^{-1} to assess its impact. When a steady state was attained, the temperature was raised stepwise per 10 °C from 200 °C to 400 °C. The temperature was held for 0.5 h in each step and the gas was analyzed. Concentrations of toluene in the inlet and outlet gases were determined using a gas chromatograph with a flame ionization detector (GC–FID). Effluent CO and CO_2 were measured with a nondispersive IR spectrometer (ADCD/7V/76/S for CO; Telaire/USA 2001 V for CO_2). The conversion (X) of toluene and the yield of CO_2 was calculated using the following equation:

$$X = \frac{I - O}{I} \times 100\%; \quad Y_{CO_2} = \frac{P_{CO_2}}{7I} \times 100\%,$$

where I is the feed rate and O is the outlet rate of toluene (mol min^{-1}). P_{CO_2} is the production rate of CO_2 (mol min^{-1}). The factor 7 in the Y_{CO_2} equation accounts for the seven carbon atoms in a toluene molecule.

2.3. Characterization of catalyst

The catalyst structure was determined using an XRD analyzer (Brookhaven Instrumental Corporation Model: APX 63/Powder) at conditions of target Cu ($\lambda = 1.5405$ Å); scanning speed 4° min^{-1}; scanning range (2θ) 20–50°. Additionally, BET surface area and the average pore diameter were measured via N_2 adsorption at liquid-nitrogen temperature using a surface area analyzer (Micromeritics ASAP 2400).