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Preparation of MnCo/MCM-41 catalysts with high performance for chlorobenzene combustion

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ABSTRACT

MCM-41 was synthesized by a soft template technique. The specific surface area and pore volume of the MCM-41 were 805.9 m^2/g and 0.795 cm^3/g, respectively. MCM-41-supported manganese and cobalt oxide catalysts were prepared by an impregnation method. The energy dispersive X-ray spectroscopy clearly confirmed the existence of Mn, Co, and O, which indicated the successful loading of the active components on the surface of MCM-41. The structure and function of the catalysts were changed by modulating the molar ratio of manganese to cobalt. The 10%MnCo(6:1)/MCM-41 (Mn/Co molar ratio is 6:1) catalyst displayed the best catalytic activity according to the activity evaluation experiments, and chlorobenzene (1000 ppm) was totally decomposed at 270 °C. The high activity correlated with a high dispersion of the oxides and was attributed to the exposure of more active sites, which was demonstrated by X-ray diffraction and high-resolution transmission electron microscopy. The strong interactions between MnO_2, Co_3O_4, $MnCoO_x$, and MCM-41 indicated that cobalt promoted the redox cycles of the manganese system. The bimetal-oxide-based catalyst showed better catalytic activity than that of the single metal oxide catalysts, which was further confirmed by H_2 temperature-programmed reduction. Chlorobenzene temperature-programmed desorption results showed that 10%MnCo(6:1)/MCM-41 had higher adsorption strength for chlorobenzene than that of single metal catalysts. And stronger adsorption was beneficial for combustion of chlorobenzene. Furthermore, 10%MnCo(6:1)/MCM-41 was not deactivated during a continuous reaction for 1000 h at 260 °C and displayed good resistance to water and benzene, which indicated that the catalyst could be used in a wide range of applications.

1. Introduction

Volatile organic compounds (VOCs) are chemicals that are defined by a saturated vapor pressure that exceeds 70 Pa at room temperature or a boiling point that is lower than 260 °C at standard pressure. They are present in haze, photochemical smog, and contribute to the greenhouse effect. They are also involved in the depletion of atmospheric ozone and the production of ground-level ozone [1,2]. In particular, chlorinated volatile organic compounds (CVOCs), which are highly toxic, are difficult to decompose in air because of the occurrence of polychlorinated byproducts, being increasingly one of the VOCs which handle hardly [3]. The CVOCs, as semi-finished chemical products, are widely used as solvents for dry cleaning and degreasing processes in industrial manufacturing [4,5].

Generally, the techniques for the destructive removal of CVOCs include high-temperature direct combustion, catalytic hydrodechlorination, catalytic steam reforming, photocatalytic oxidation, and catalytic combustion. Compared with other techniques, catalytic combustion is applied in a wide range of applications because of its lower energy consumption, lower handling temperature, and higher purification efficiency.

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For the catalytic combustion of CVOCs, catalyst support materials with a large specific surface area and pore volume, which are beneficial for the dispersion of the active substances, are always prevalent. They usually consist of molecular sieves (such as γ-Al_2O_3, HFAU, HZSM-5, MCM-41), metal oxides, and honeycomb ceramics [3]. Compared with other two supports, molecular sieves not only have better thermal stability, but also possess higher specific surface areas and more acidic sites [6]. However, the problem of carbon deposition is yet to be solved. As a nanostructured material, MCM-41 with a hexagonal ordered pore arrangement and large adsorption quantity was first discovered in 1992 [7]. It has been widely applied in resid catalytic cracking, heavy oil catalytic hydrogenation, alkyl isomerization, and macromolecular fine chemicals. Furthermore, it is completely composed of silica and has no acidity, effectively avoiding the issue of carbon deposition.

Currently, the catalysts used for the destruction of CVOCs can be classified into two types according to their active components, including noble metals catalysts [8–10] and non-noble metal catalysts. In practice, noble-metal-based catalysts show higher activity. However, they are more expensive and undergo deactivation because of chlorine poisoning and the formation of polychlorinated compounds. Therefore, many efforts have been devoted to the synthesis of transition-metal oxide catalysts [11–16] because they resist deactivation to a larger extent and are cheaper. Usually, metal oxides (such as V_2O_5, Cr_2O_3, MnO_2, Co_3O_4 and NiO) or composite metal oxides are used as active components of transition metal oxide catalysts. In particular, manganese and cobalt oxides possess better activity, lower cost, and create little or no environmental pollution. Therefore, they have been widely used both domestically and internationally [17,18]. However, when use only one component, the loss of active sites (which could adsorb HCl and/or Cl_2) or the formation of volatile species (metal chloride or metal chloride oxide) at lower temperature may cause partial deactivation of these transition metal oxides catalysts, which may restrict the applications of transition metal oxides catalysts [19]. Thus, composite metal oxides catalysts have been reported, which improve the mobility of the surface-active oxygen and increase the surface acidic sites through the synergistic effect of the metal-metal and metal-support interactions.

There have been numerous reports of molecular-sieves-supported transition-metal oxides as catalysts that have been used to eliminate CVOCs [20–27]; for example, Cu-ZSM-5 [26] and Cr_2O_3-CuO/HZSM-5 [27]. Furthermore, the MCM-41 as a catalyst support, its applications for the destruction of CVOCs have also been reported, including Pt/P-MCM-41, La/MCM-41, Ce/MCM-41, and Pt/MCM-41, which showed a high catalytic performance [28–30]. In the catalytic combustion field of CVOCs, there are rarely reports about MCM-41 supported MnCo catalysts for destruction of chlorobenzene (CB). Therefore, we synthesized MCM-41-supported MnCo catalysts for CB combustion.

In this paper, we prepared MCM-41-supported MnCo catalysts, and explored their catalytic performance for combustion of CB in air. Furthermore, the synergistic effect between Mn (the main active phase), Co (the second active phase) and MCM-41 was studied. The catalysts were analyzed by X-ray diffraction (XRD), high-resolution transmission electron microscopy (HRTEM), and energy dispersive X-ray spectroscopy (EDS), nitrogen (N_2) adsorption-desorption, temperature-programmed reduction of hydrogen (H_2-TPR), and temperature-programmed desorption of CB (CB-TPD). Furthermore, the activity and durability of the materials was evaluated to further investigate the performance of the catalysts.

2. Experimental

2.1. *Synthesis*

The MCM-41 was prepared according to the following procedure. Tetrabutylammonium silicate (TBAS) was obtained from tetrabutylammonium hydroxide (TEAOH, 40 wt%, Aldrich) and fumed silica (Sigma) in a 10:1 ratio. Then, 12.21 g of TBAS was combined with 20.3 g of cetyltrimethylammonium chloride (CTAC, 25 wt%, Aldrich) and 5.94 g of H_2O under stirring, followed by the addition of 5.91 g of fumed silica. The resulting gel was placed in a Teflon bottle and heated for 120 h at 100 °C to perform the crystallization. After cooling to room temperature, the solid product was recovered by filtration, washed thoroughly with deionized water, and dried in an oven at 80 °C overnight. Finally, the template CTAC was removed by calcination in a stream of air at 550 °C for 5 h [31]. A series of MnCo/MCM-41 catalysts with different molar ratios of Mn/Co (3:1, 6:1, and 9:1) were prepared by co-impregnation of MCM-41 with an aqueous solution of $Mn(NO_3)_2$ (50%) and $Co(NO_3)_3\cdot 6H_2O$ overnight. Then, the samples were stirred in the electrothermal setup until desiccation. Later, calcination was performed at 500 °C for 2 h. The particles with a 40–60 mesh size were sieved to obtain the products. The total content of the single metal (Mn or Co) and mixed MnCo (the sum of both Mn and Co) for all the catalysts was10 wt%.

2.2. *Catalytic activity test*

The activity evaluation of the catalysts (350 mg) was performed in a WFS-3010 microreactor (Xianquan, Tianjin, China), in which the space velocity was 20000 h^{-1} and the concentration of CB was 1000 ppm. The concentration of O_2 in the gas flow stream was 21%. The on-line measurements were conducted using a Shimadzu GC-14 (Japan), which had a flame ionization detector (FID). The temperatures of the vaporizer and column were both 120 °C. The data were obtained and analyzed using a N2000 chromatography data workstation. The degradation products were detected by mass spectrometry (MS, QGA, Hiden, UK). No byproducts other than H_2O, CO_2, and HCl were detected. Thus, the conversion was calculated based on CB consumption. The durability of the catalysts for CB combustion was also investigated under the same conditions.

2.3. *Characterization*

The composition of the catalyst phase was determined by XRD, which was performed with a PANalytical EMPYREAN