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Article (Special Issue on Environmental Catalysis and Materials)

Low-temperature catalytic oxidation of formaldehyde over Co_3O_4 catalysts prepared using various precipitants



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ARTICLE INFO

Article history:

Received 31 January 2016

Accepted 23 March 2016

Published 5 June 2016

Keywords:

Formaldehyde oxidation

Catalysis

Cobalt oxide

Precipitation method

Potassium ion

ABSTRACT

Co_3O_4 catalysts prepared with different precipitants ($\text{NH}_3\cdot\text{H}_2\text{O}$, KOH , NH_4HCO_3 , K_2CO_3 and KHCO_3) were investigated for the oxidation of formaldehyde (HCHO). Among these, KHCO_3 -precipitated Co_3O_4 ($\text{KHCO}_3\text{-Co}$) was the most active low-temperature catalyst, and was able to completely oxidize HCHO at the 100-ppm level to CO_2 at 90 °C. *In situ* diffuse reflectance infrared spectroscopy demonstrated that hydroxyl groups on the catalyst surface were regenerated by K^+ and CO_3^{2-} , thus promoting the oxidation of HCHO. Moreover, H_2 -temperature programmed reduction and X-ray photoelectron spectroscopy showed that employing KHCO_3 as the precipitant increased the $\text{Co}^{3+}/\text{Co}^{2+}$ molar ratio on the surface of the Co_3O_4 catalyst, thus further promoting oxidation. Structural characterization revealed that catalysts precipitated with carbonate or bicarbonate reagents exhibited greater specific surface areas and pore volumes. Overall, these data suggest that the high activity observed during the Co_3O_4 catalyzed oxidation of HCHO can be primarily attributed to the presence of K^+ and CO_3^{2-} on the Co_3O_4 surface and the favorable $\text{Co}^{3+}/\text{Co}^{2+}$ ratio.

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1. Introduction

Formaldehyde (HCHO) was classified as a human carcinogen by the International Agency for Research on Cancer in June 2004 [1]. Long-term exposure to parts per million (ppm) HCHO concentrations thus represents a health hazard, and the short-term (30 min) exposure limit recommended by the World Health Organization is 0.1 mg/m^3 [2]. HCHO is released from various products, such as chipboard, textiles, and decorative materials, and can also contribute to the formation of photochemical smog [3]. Many efforts have been made to devise methods of reducing indoor HCHO concentrations to satisfy the stringent environmental regulations [4–6]. Conventional absorbents (such as activated carbon) are a ready means of eliminating HCHO, but the associated challenges of waste disposal and frequent replacement cannot be ignored. Photocatalysis

allows the ongoing degradation of low HCHO concentrations, although the limited capacity of this approach and the inevitable formation of undesirable by-products restricts its practical application [7]. As such, high efficiency, low-temperature catalytic oxidation is believed to represent the most promising technology for HCHO removal [8,9].

Initially, supported noble metal catalysts were applied to HCHO oxidation at room temperature [10–13], but the high cost of these metals restricts their large-scale application. Fortunately, oxides of transition metals, including Mn, Co, and Cu, also exhibit outstanding catalytic performance for low-temperature HCHO oxidation. Among these, Co_3O_4 has been widely investigated as a component of heterogeneous catalysts because of its high performance [12–18]. Many researchers have found that the catalytic activity of Co_3O_4 varies depending on the method used to prepare the catalyst. Zhu et al. [19] synthe-

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This work was supported by the National Natural Science Foundation of China (21577088).

DOI: 10.1016/S1872-2067(15)61086-5 | <http://www.sciencedirect.com/science/journal/18722067> | Chin. J. Catal., Vol. 37, No. 6, June 2016

sized a material consisting of Co_3O_4 supported on ZSM-5 ($\text{Co}_3\text{O}_4/\text{ZSM-5}$) for the oxidation of propane, using impregnation (IM), deposition precipitation (DP), and hydrothermal (HT) methods. The catalytic activities of the resulting materials were in the order of $\text{HT} > \text{DP} > \text{IM}$, and it was also determined that the catalyst prepared with ammonium bicarbonate as the precipitant was superior to one prepared with NaOH. Shi et al. [20] produced a $\text{Mn}_x\text{Co}_{3-x}\text{O}_4$ catalyst for HCHO oxidation as a solid solution via both co-precipitation and citric acid methods. They found that the sample prepared by co-precipitation exhibited the best catalytic performance and was able to completely oxidize HCHO at 75 °C. The addition of specific alkali elements, such as K and Na, has also proven to be effective for promoting the catalytic oxidation of HCHO, by increasing the concentration of OH^- on the catalyst surface [21–23].

The precipitation method is popular and also practical with regard to eventual scaled-up applications. Therefore, it is necessary to both research and develop the synthesis of transition metal-based catalysts utilizing different precipitation methods. It would also be beneficial to further research the effect of the precipitation method on catalyst performance for low-temperature HCHO oxidation. Therefore, in the present study, various precipitants were used to generate Co_3O_4 catalysts, and the effects of these precipitants on the subsequent HCHO oxidation performance were discussed.

2. Experimental

2.1. Catalyst preparation

All chemicals used in this work were analytical grade and were purchased from the Sinopharm Chemical Reagent Co. (SCRC). The $\text{NH}_3\text{-Co}$, KOH-Co , $\text{NH}_4\text{HCO}_3\text{-Co}$, $\text{K}_2\text{CO}_3\text{-Co}$, and $\text{KHCO}_3\text{-Co}$ catalysts were prepared using a precipitation method, employing five precipitants: $\text{NH}_3\text{-H}_2\text{O}$, KOH , NH_4HCO_3 , K_2CO_3 , and KHCO_3 . In this method, a solution of the chosen precipitant (2 mol/L) was added dropwise (10 mL/min) to a solution of $\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ (100 mL, 0.1 mol/L) with rapid stirring at room temperature until the reaction solution had a pH value of 9. After standing for 4 h, the resulting precipitate was removed by filtration and washed with deionized water until the wash water was neutral, then dried at 100 °C for 10 h and calcined at 400 °C for 2 h. For comparison purposes, a sample designated as PC/AHC-Co was prepared by dispersing $\text{HN}_4\text{HCO}_3\text{-Co}$ in a K_2CO_3 solution (2 wt%) with stirring for 30 min, followed by drying of the resulting product overnight at 100 °C.

2.2. Catalyst characterization

All samples were pretreated at 200 °C for 1 h prior to catalytic trials. X-ray diffraction (XRD) patterns of the catalysts were acquired using a D8 ADVANCE (Bruker) X-ray diffractometer with $\text{Cu K}\alpha$ radiation. The K content of each sample was determined by atomic absorption spectroscopy (AAS). N_2 adsorption-desorption isotherms were obtained using the Barrett-Joyner-Halenda (BJH) method with a TriStar II 3020 appa-

ratus (Micromeritics) and X-ray photoelectron spectroscopy (XPS) spectra were acquired on an AXIS Ultra DLD instrument (Kratos) at 300 W using $\text{Mg K}\alpha$ excitation. H_2 temperature-programmed reduction (TPR) data were obtained with a Chemisorb 2720 TPX apparatus (Micromeritics). In these tests, a 0.1-g sample (40–60 mesh) was pretreated under a N_2 flow at 400 °C for 30 min in a quartz reactor. The cooled sample was subsequently reduced under a flow (40 mL/min) of 5 vol% H_2 in Ar from 20 to 700 °C (10 °C/min). *In situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) data were acquired on a Nicolet 6700 FTIR spectrometer equipped with an MCT detector and a DRIFTS cell (Harrick), scanning from 4000 to 800 cm^{-1} with a resolution of 4 cm^{-1} . Samples (30 mg) were assessed under a flow of 100 ppm HCHO and 21 vol% O_2 in N_2 at 100 mL/min total flow. Prior to the FTIR characterization, catalysts were pretreated under N_2 for 1 h at 300 °C.

2.3. Catalytic activity measurements

Catalytic reactions were carried out in a U-shape fixed-bed quartz tubular reactor with an inner diameter of 4 mm. The catalyst sample (100 mg, 40–60 mesh) was placed between two quartz wool layers in the tube and mass flow controllers were used to set the gas flow rates. HCHO vapor was obtained by passing a flow of N_2 through a paraformaldehyde (99%, SCRC) solution in a container within a water bath. The concentration of HCHO was adjusted by varying the N_2 flow rate and/or the temperature of the water bath. By mixing this N_2 stream with a flow of O_2 in N_2 , a typical feed gas composition (100 mL/min, GHSV of 69000 h^{-1}) containing 100 ppm HCHO and 21 vol% O_2 was obtained.

The concentrations of CO and CO_2 in the outgoing gas stream were measured by gas chromatography (GC 9560, HUAAI, flame ionization detector with a CH_4 conversion oven, 5 Å molecule sieve and TDX-01 packed columns). Experimental data were recorded beginning at the point at which the reaction stabilized at each reaction temperature and data acquisition continued over the span of 1 h. The HCHO conversion values were calculated using the equation

$$\text{HCHO conversion} = \frac{[\text{CO}_2]_{\text{out}}}{[\text{HCHO}]_{\text{in}}} \times 100\%$$

where $[\text{CO}_2]_{\text{out}}$ is the CO_2 concentration in the outlet stream (vol%), and $[\text{HCHO}]_{\text{in}}$ is the inlet HCHO concentration (vol%).

3. Results and discussion

3.1. Catalytic activity

Figure 1 summarizes the catalytic activities during HCHO oxidation over different catalysts. It is evident that 100% of the HCHO was oxidized to CO_2 over the $\text{KHCO}_3\text{-Co}$ and PC/AHC-Co at 90 °C, and so these two catalysts had the best low-temperature activity in this study. In contrast, the KOH-Co and $\text{NH}_3\text{-Co}$ catalysts achieved 100% HCHO conversion at 120 and 130 °C, respectively. The light off temperature (T_{10}) obtained with the $\text{KHCO}_3\text{-Co}$ was only 60 °C, much lower than the values for the $\text{NH}_4\text{HCO}_3\text{-Co}$ (90 °C) and $\text{NH}_3\text{-Co}$ (110 °C). The PC/AHC-Co performance was significantly better than that of the

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