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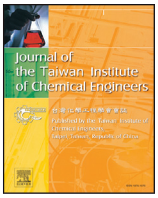

Catalytic oxidation of ethyl acetate over CuO/ZSM-5 catalysts: Effect of preparation method

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ABSTRACT

A series of CuO/ZSM-5 catalysts with different copper loadings were prepared by impregnation (IM) and chemical vapor deposition (CVD) methods, respectively. Their physicochemical properties were investigated by N_2 adsorption/desorption, X-ray diffraction (XRD), transmission electron microscopy (TEM), X-ray photoelectronic spectra (XPS), temperature-programmed reduction by hydrogen (H_2-TPR) and temperature-programmed desorption of NH_3 (NH_3-TPD). The XRD and TEM results demonstrated that the crystallite size of the CuO prepared by CVD method was smaller than that by IM, and the XPS results illustrated that the copper specie was mostly in Cu^{2+} state and Cu^{+} co-existed. The performance of catalytic oxidation of ethyl acetate was conducted in the fixed-bed reactor based on CuO/ZSM-5 catalysts. The experimental results showed that the preparation method affected the catalytic activity of CuO/ZSM-5; the CVD catalysts exhibited a higher catalytic activity for ethyl acetate oxidation compared with the IM catalysts at the same copper loadings. Ethanol and acetaldehyde are observed to be the intermediate products in the combustion of ethyl acetate over the synthesized catalysts. The relative amounts of acetaldehyde and ethanol are determined by the selectivity of the catalyst toward acetaldehyde production from ethanol. Particularly, the 3 wt% CVD catalyst showed the best catalytic activity for ethyl acetate oxidation with 90% conversion of ethyl acetate at 235 °C, which was much lower than that of the 3 wt% IM catalyst (278 °C), meanwhile, the intermediate products of the 3 wt% CVD for ethyl acetate oxidation were completely oxidized into CO_2 and H_2O at temperature as low as 288 °C.

1. Introduction

Volatile organic compounds (VOCs) are a group of major environmental pollutants emitted from human activities, petrochemical industry, pharmaceutical industry, surface corrosion, paint decoration industry and printing industry [1,2]. These volatile organic compounds, which are responsible for the stratospheric depletion, tropospheric ozone formation, smog information, climate change and carcinogenic effects in humans, are a class of compounds with various types, complex ingredients and wide range of sources [3,4]. As most of the countries have enacted a strict legal system to limit VOCs emissions, there are many researchers seeking highly efficient, low energy consumption technologies to meet the standards [5].

Catalytic oxidation based on low operation temperature, wide range of applications, high purification efficiency and environmental benefits is the most widely used techniques for handling VOCs compared with the traditional methods [6]. The active components of the catalyst can be broadly classified into two categories: noble metal catalysts [7–9] and transition metal oxide catalysts [10–13]. Noble metals exhibit excellent efficiency and activity in the purification of VOCs at low temperatures, but the high manufacturing cost and low thermal stability limit their commercial application [5,14]. As for transition metal oxides, which present low activity but have the advantages of excellent stability, masking tolerance, long lifetime and low cost compared with noble oxides [15,16]. Among the transition metal oxide catalysts, copper oxide is considered to be one of the catalysts with the highest catalytic activity for the total oxidation of VOCs [5,11].

Moreover, the physicochemical properties of the support materials play a critical role in the catalytic performance of the catalysts, which can improve the dispersion of the active component on the support surface or determine the oxidation state and thus enhancing the activity of the catalysts. Among the available support materials, zeolites have been employed as promising support in various catalysts for the combustion of VOCs due to their pore structures, corrosion resistance, ion exchange properties and acidic properties [17,18]. Commonly used zeolites can be roughly divided into mesoporous [16,19] (MCM-41, SBA-15) and microporous zeolites [6,18,20,21] (ZSM-5) according to the size of pore channels.

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ZSM-5 zeolite possesses a high specific surface area, uniform pore structure, high acidity, and good chemical stability, which is beneficial to the removal of volatile organic compounds [20]. Ou et al. [22] found that the microwave-assisted secondary growth synthesis can effectively prepare ZSM-5 coating on SiC foam with the uniform coating thickness. Li et al. [20] reported the ZSM-5 zeolite was used as structured support for volatile organic compounds oxidation and the catalysts obtained presented outstanding catalytic activity and superior stability in ethyl acetate complete oxidation.

The preparation method also affects the morphology of the catalysts, thus altering the pore structure and affecting the catalytic activities [6]. Various preparation methods can be applied in scientific research including co-precipitation [23], ion exchange [24], impregnation [25] and chemical vapor deposition method [26–28]. As a result of the advantages of simple operation, low cost, high utilization rate and suitable for most zeolites, impregnation is the most widely used way of supporting the active component of the catalyst as a traditional method. However, the disadvantage is that the active components are mainly distributed on surface of the support and the migration of active components leads to uneven distribution thus affecting the catalytic activity [29]. Chemical vapor deposition (CVD) has proven to be a cost-effective and single-step gas-phase preparation technique. According to the literatures [29–32], the enhanced activity was attributed to the fact that the gas-phase process enables the highly dispersed ability of the active ingredient, independent of the nature of the support material and stronger interaction with the support material. Therefore, the CVD method is a promising technique for preparing catalysts via depositing active phases from gaseous metal precursors into porous materials. Assebban et al. [27] utilized pulsed spray evaporation chemical vapor deposition to prepare cobalt oxide catalyst with clay as the support for the treatment of unsaturated hydrocarbons. The results revealed that cobalt oxide crystals are uniformly supported on the surface of the clay and the catalyst has excellent catalytic activity, which is due to a synergistic interaction between the cobalt oxide films and the clay. Bahlawane et al. [32] investigated the catalytic activity of Co_3O_4 catalysts prepared by CVD for methane combustion, the results showed that monolithic cordierites with low specific surface area were uniformly coated with cobalt oxide thin films on controlled thickness using the CVD process and these films exhibit a remarkably high efficiency.

Ethyl acetate is one of the typical ester compounds and gaseous pollutant that predominantly existed in various industrial processes and emitted into the atmosphere without prior further purification. In the present study, little attention has been focused on the research of CuO/ZSM-5 catalysts prepared by the CVD method as the potential catalysts for ethyl acetate combustion. Therefore, CuO/ZSM-5 catalysts were synthesized for ethyl acetate combustion to investigate the catalytic efficiency of these different catalysts. The main purposes of this study were to (1) compare the physicochemical properties of CuO/ZSM-5 catalysts prepared by the IM and CVD method; (2) investigate the effect of preparation method on the performance of ethyl acetate over these catalysts, including analyzing the conversion of ethyl acetate into intermediate products.

2. Experimental

2.1. Materials

Columnar ZSM-5 with an atomic Si/Al ratio of 50 was purchased from The Catalyst Plant of Nankai University (Tianjin, China). Copper acetylacetonate ($Cu(acac)_2$) was obtained from Aladdin Industrial Corporation (Shanghai, China). Copper nitrate ($Cu(NO_3)_2 \bullet 3H_2O$, >99.0%) was purchased from Guangzhou Chemical Regent Factory (Guangzhou, China). Ethyl acetate ($C_4H_8O_2$, ≥ 99.5%) and ethanol (C_2H_5OH, >99.7%) were supplied by Guangdong Guanghua Technology Co., Ltd (Guangzhou, China).

2.2. Catalyst preparation

The metal oxides modified ZSM-5 catalysts with the corresponding copper loadings of 1, 3, 5, 10 wt% were prepared by impregnation (IM) and chemical vapor deposition (CVD) methods, respectively. The IM catalysts were prepared as follows: known amounts of copper nitrate was added to deionized water and mixed with 4 g of ZSM-5 granular at room temperature, and the excess moisture was removed in an oven at 100 °C until dryness and stirred several times in the process. Finally, the samples were dried at 100 °C for 12 h. The CVD catalysts were synthesized as follows: copper supported on ZSM-5 zeolite was synthesized by chemical vapor deposition using copper acetylacetonate ($Cu(acac)_2$) and ZSM-5 as copper source precursor and target substrate, respectively. A known amount of $Cu(acac)_2$ was sublimed at 180 °C and deposited at 350 °C under a static nitrogen atmosphere in a sintering furnace (Hefei Kejing Material Technology co., LTD). By varying the amounts of copper of 1, 3, 5 and 10 wt%, four samples with different copper loadings were prepared. All catalysts were calcined at 550 °C for 4 h under static air in a muffle furnace. In order to evaluate the catalytic activity, the cylindrical catalyst was previously pelletized and sieved to 40–60 meshes (300–450 μm).

2.3. Catalyst characterization

X-ray diffraction patterns (XRD) of samples recorded on a D8 Advance (Bruker Co.) diffractometer with a X-ray diffractometer using Cu Kα radiation operated at 40 kV and 40 mA in the 2θ range of 5–80° with a 2θ step size of 1° and a step time of 10 s. In addition, the average crystallite sizes of CuO in CuO/ZSM-5 catalysts are calculated from CuO diffraction peak by the Scherrer equation [27,33]:

$$D = \frac{K\lambda}{\beta cos\theta} \tag{1}$$

where K is a Scherrer constant related to crystallite shape, normally considered as 0.89, λ is X-ray wavelength ($\lambda = 0.154056$ nm), β is the peak width of the diffraction peak profile at half maximum height, θ is the diffraction angle.

The transmission electron microscopy (TEM) images of samples were obtained on a JEM 2100 electron microscope operated at 200 kV. The actual loading of the catalyst was measured using atomic absorption spectrophotometry (AA240FS, Varian Co., USA). Samples of about 0.1 g were dissolved in acidic solution (42% HNO_3) overnight, and diluted at a certain concentration and then detected by atomic absorption spectrophotometry.

The nitrogen adsorption and desorption isotherms were measured on a 3H-2000PS1 instrument in static measurement mode. The samples were degassed at 200 °C for 2 h before measurement. The BET specific area of the samples were calculated according to Brunauer–Emmett–Teller (BET) method and the total pore volume was calculated by the analysis of N_2 adsorption–desorption isotherms, the micropore volume was calculated by HK (Horvath–Kawazoe) method whereas the adsorption average pore diameter was determined by the BJH (Barrett–Joyner–Halenda) method.

The X-ray photoelectron spectroscopy (XPS) experiments were recorded on a Kratos Axis Ultra (DLD) spectrometer using an Al Kα (1486.6 eV) radiation source operated at 15 kV and 10 mA. The carbonaceous C1s line (284.6 eV) was used as a reference to calibrate the binding energy (BE).

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