Full Length Article

The catalytic oxidation of formaldehyde over palygorskite-supported copper and manganese oxides: Catalytic deactivation and regeneration

Peng Liu[a,c,d], Gaoling Wei[b], Hongping He[a,c,d], Xiaoliang Liang[a,c,d,*], Hanlin Chen[a,c,d], Yunfei Xi[e], Jianxi Zhu[a,c,d]

[a] CAS Key Laboratory of Mineralogy and Metallogeny/Guangdong Provincial Key Laboratory of Mineral Physics and Materials, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, PR China
[b] Guangdong Key Laboratory of Integrated Agro-Environmental Pollution Control and Management, Guangdong Institute of Eco-Environmental Science & Technology, Guangzhou 510650, PR China
[c] Institutions of Earth Science, University of Chinese Academy of Sciences, Beijing 100049, PR China
[d] University of Chinese Academy of Sciences, Beijing 100049, PR China
[e] School of Earth, Environmental and Biological Sciences, Queensland University of Technology (QUT), 2 George Street, Brisbane, Queensland 4001, Australia

A R T I C L E   I N F O

A B S T R A C T

The emission of volatile organic compounds (VOCs) from industrial and commercial processes is detrimental to human health and the environment. Though numerous catalysts have been reported to eliminate the pollution of VOCs, their deactivation and regeneration are still largely unknown. In this study, the prepared palygorskite-supported Cu-Mn oxides displays slight decrease of catalytic activity in the initial stage of formaldehyde oxidation. After the thermal treatment of spent catalyst at 400 °C, the catalytic activity is partially recovered. A deactivation and regeneration mechanism is proposed, based on the stability test and the comprehensive characterizations of fresh and spent catalysts. The accumulation of formate species and the depletion of oxygen on the surface of Cu-Mn oxides are responsible for the decline of activity. Thermal treatment of deactivated catalyst at 400 °C recovers the catalytic activity because it gasifies the carbonaceous intermediates and replenishes surface oxygen. The obtained results will be of great significance for the application of transition metal oxide-based catalysts in the abatement of VOCs.

1. Introduction

Volatile organic compounds (VOCs) emitted from industrial and commercial processes are not only precursors of secondary aerosol, ozone, and photochemical smog, but are also carcinogenic and teratogenic substances to human health [1,2]. Compared to the common technologies for the elimination of VOCs (e.g., adsorption [3], condensation [4], and photo-catalysis [5]), catalytic oxidation is a promising alternative for high removal efficiency, low operation temperature, and less secondary pollutants [6]. Developing effective catalysts for the deep oxidation of VOCs has drawn much attention in recent years.

However, great efforts are still needed to be made to enhance catalytic activity, selectivity of CO_2, and stability of catalysts. Among these, the deactivation of catalyst, which would give rise to the decrease of catalytic activity, selectivity, and lifetime, is the primary challenge associated with the real application [7]. In literature, several deactivation mechanisms for specific catalysts have been proposed, such as poisoning, surface chemical transformation, and sintering [8]. For instance, H_2O has a serious poisoning effect on CeO_2-based catalysts for the elimination of VOCs, related to the steric blockage of adsorption-oxidation sites and disablement of surface oxygen [9]. Halogen ions (e.g., F^-, Cl^-, Br^- and I^-) deactivate the supported precious metals by forming coordination bonds with surface precious metal atoms (e.g., Pt, Au and Ag) [10]. For transition metal oxides with multiple valences (e.g., Co_2O_3, CuO and Mn_2O_3), the deactivation results from both the chemical transformation of catalyst surface and even bulk phase, and the variation of textural properties by redox processes [11].

Based on the distinct deactivation mechanisms, several efficient methods have been developed to recover activity or to fabricate catalyst with high stability, including the addition of more tolerant components [8,12], and a slight increase of reaction temperature to remove

poisonous species [9]. Thermal treatment is a conventional strategy to reactivate the catalyst on which the carbonaceous intermediate or coke is formed [13]. Carbon or coke blocking the active sites is easy to gasify into CO_2 under nitrogen, water or oxygen, exposing the active sites again [14]. For instance, the presence of water vapor and hydroxyl groups on catalyst surface contributes to the decomposition of dioxymethylene, formate, and carbonate species, and thus, promotes the oxidation of formaldehyde (HCHO) [15,16]. Thermal treatment is similar to chemical looping combustion, where the oxygen carrier releases oxygen through decomposition in a fuel reactor, and then is regenerated in an air reactor [17]. However, the effect of thermal treatment temperature on the regeneration of surface or lattice oxygen still needs investigation. Moreover, thermal treatment under higher temperature results in the sintering of catalyst, while treatment at lower temperature could not thoroughly recover the surface or lattice oxygen. Calcinations at an optimized temperature not only avoid the aforementioned drawbacks, but also save the cost on energy or the replacement of catalyst.

Due to the merits of low cost, considerable reducibility, and superior resistance to chloride and sulfur poisoning [18,19], transition metal oxide based catalysts (e.g., MnO_x, CuO, Fe_2O_3 and Co_3O_4) are regarded as promising candidates for VOCs oxidation. The combination of two or more transition metal oxides is a novel strategy to improve the catalytic performance, owing to the synergetic effect derived from fast electron or oxygen transfer between coupled oxides [20,21]. Pal is an ideal support with abundant resource, large surface area ($> 200\,m^2\,g^{-1}$), high thermal and chemical stability, plentiful nanopores, and plenty of solid acid sites [22,23]. In previous study, the Cu-Mn oxides, which was amorphous in structure, were supported on Pal to improve the dispersion of active components against sintering during thermal treatment [24]. The amorphous Cu-Mn oxides loaded on Pal were confirmed to be spinel-like structure which was constructed by CuO_4 tetrahedra and MnO_4 octahedra. The Pal-supported Cu-Mn oxides achieved 90% CO_2 generation in the formaldehyde oxidation at 207–258 °C. However, after three consecutive runs from 150 to 350 °C, the catalyst slightly deactivated with CO_2 conversion at 200 °C decreasing from 86.0% to 69.9%.

In this study, the deactivation mechanism of Pal-supported Cu-Mn oxide was investigated from the viewpoint of sintering, structure variation, and surface transformation, verified by the systematic characterization of fresh and spent catalysts. According to the proposed deactivation mechanism, improvement in catalytic activity has been further achieved by a slight increase of calcination temperature for spent catalyst.

2. Experimental

2.1. Catalyst preparation

Pal-400 was derived from Mingguang City, Anhui Province, China, purified by sedimentation, acid wash and sieving (mesh width at 74 μm), and calcined at 400 °C. The Pal-supported Cu-Mn oxide catalyst was prepared by an impregnation method. 4 mL of $Cu(NO_3)_2 \cdot 3H_2O$ solution (2.0 mol L^{-1}) and 4 mL of $Mn(NO_3)_2 \cdot 6H_2O$ solution (2.0 mol L^{-1}) were sequentially introduced into Pal suspension (200 g L^{-1}, 50 mL) under vigorous stirring. Then 32 mL of ammonia solution (1.5 mol L^{-1}) was added dropwise into the above suspension while stirring at 80 °C. The precursor was calcined at 400 °C in muffle finance for 2 h. The obtained sample was labeled as 5Cu5Mn, with chemical composition shown in Table S1. For comparison, reference samples of 10Cu0Mn with 9.7 wt% of Cu and 0Cu10Mn with 10.3 wt% of Mn were prepared by following the above procedures except the addition of $Mn(NO_3)_2 \cdot 6H_2O$ and $Cu(NO_3)_2 \cdot 3H_2O$, respectively. Through careful observation of phase composition by high-resolution TEM, the Cu-Mn oxides on Pal displayed spinel-like structure (Fig. S1).

2.2. Catalyst characterization

The phase structures of fresh and spent catalysts were analyzed by X-ray diffraction (XRD, Bruker D8 advance) using Cu Kα radiation at a scan rate of 2° min^{-1}. The morphology was observed by transmission electron microscope (TEM, JEOL JEM-2100F) operated at 200 kV. The element composition was characterized by PerkinElmer AAnalyst 400 Flame Atomic Absorption Spectrometry. The BET specific surface area was measured on Micromeritics ASAP 2020. The pore size distribution and mesoporous volume was obtained from the desorption branch via BJH method. The oxidation state of Mn and Cu was determined by X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha) with the binding energy referenced to C 1s at 284.8 eV. Temperature programmed oxidation (TPO) measurement was carried out from room temperature to 600 °C at a rate of 5 °C min^{-1} under dry air. The samples were pretreated at 100 °C to remove the physically adsorbed species. The CO_2 generation was analyzed with a non-dispersive infrared analyzer. Temperature programmed reduction (TPR) measurement was performed on Builder PCA-1200 equipped with a TCD detector. *In situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was conducted on a Bruker Vertex-70 infrared spectrometer equipped with a gas flow system and high-temperature controllable cell (Harrick, Praying Mantis) with ZnSe windows. The temperature was increased from 30 to 350 °C at a rate of 5 °C min^{-1}.

2.3. HCHO oxidation

The periodic steady-state HCHO oxidation over as-prepared catalysts was performed on a fixed-bed reactor with continuous flow at atmospheric pressure. 100.0 mg of catalyst was loaded in a quartz tube reactor with an internal diameter of 6 mm. The HCHO in feed stream was obtained by flowing N_2 into paraformaldehyde at 39 °C. The inlet gas was composed of 1000 ppm HCHO and 20 vol% oxygen balanced by N_2. The total flow rate was set at 100 mL min^{-1}, corresponding to a gas hourly space velocity (GHSV) of 32 500 h^{-1}. To investigate the resistance of catalyst to moisture, water was introduced into the feed gas with a syringe pump, and a heater was attached on the gas line to avoid the condensation of water and polymerization of HCHO. The concentration of CO_2 in outlet gas (A_t) was analyzed after 1 h by a non-dispersive infrared CO_2 analyzer (Beijing Huayun GXH-3010E), while the concentration of HCHO was analyzed by an acetylacetone method (GB/T15516-1995, China). The HCHO in outlet gas was absorbed by water, then reacted with acetylacetone at pH = 6 under boiling water bath, and completely converted to a stable yellow compound, 3,5-diacetyl-1,4-ditydro-1,4-dihyrolutidine (DDL). The concentration of DDL was analyzed by PE Lambda 850 UV–Vis spectrophotometer at a wavelength of 413 nm. HCHO conversion efficiency was calculated by $(1 - C_t/C_0) \times 100\%$, where C_t and C_0 were the concentration of HCHO in outlet gas and inlet gas, respectively. CO_2 generation efficiency was expressed as $(A_t/A_0) \times 100\%$, where A_0 was the theoretical CO_2 concentration when HCHO in the inlet gas was completely oxidized. After the stability test, the spent catalyst was collected and designated as 5Cu5Mn-*x*, where *x* represented reaction temperature. The 5Cu5Mn-*x*-R was the spent catalyst of 5Cu5Mn-*x* regenerated at 400 °C for 2 h under air without HCHO. The 5Cu5Mn-250–24 h was the spent catalyst having performed at 250 °C for 24 h.

3. Results and discussion

3.1. Catalytic deactivation

The activity of 5Cu5Mn and reference samples was tested for HCHO oxidation. To check whether HCHO was decomposed spontaneously, a blank test was carried out without catalyst, where no CO_2 generation was observed. Pal-400 displayed mild catalytic activity, achieving approximately 40% of CO_2 generation at 350 °C (Fig. S2). The catalytic