Applied Clay Science 161 (2018) 265–273

Contents lists available at ScienceDirect

Applied Clay Science

journal homepage: www.elsevier.com/locate/clay

Research paper

Synergetic effect of Cu and Mn oxides supported on palygorskite for the catalytic oxidation of formaldehyde: Dispersion, microstructure, and catalytic performance

Peng Liu[a,b,d], Gaoling Wei[c], Xiaoliang Liang[a,d,*], Dong Chen[b,**], Hongping He[a,d], Tianhu Chen[b], Yunfei Xi[e], Hanlin Chen[a,d], Donghui Han[f], Jianxi Zhu[a,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] School of Resources and Environmental Engineering, Hefei University of Technology, Hefei 230009, PR China
[c] Guangdong Key Laboratory of Integrated Agro-Environmental Pollution Control and Management, Guangdong Institute of Eco-Environmental Science & Technology, Guangzhou 510650, PR China
[d] University of Chinese Academy of Sciences, Beijing 100049, PR China
[e] School of Earth, Environmental and BiologicalSciences, Queensland University of Technology (QUT), 2 George Street, Brisbane,Queensland 4001, Australia
[f] South China Institute of Environmental Sciences, the Ministry of Environment Protection of PRC, Guangzhou 510655, PR China

ARTICLE INFO

Keywords:
Volatile organic compounds
Palygorskite
Catalytic oxidation
Spinel Cu–Mn oxides
In situ DRIFTS

ABSTRACT

In this study, palygorskite (Pal), a natural nanorod-like clay mineral, is applied as the support of mixed Cu–Mn oxides for formaldehyde (HCHO) oxidation, with focus on their dispersion, microstructure, and relative role during the catalytic oxidation. The composite material loaded with Cu–Mn oxides retains the nanorod-like morphology of Pal, while the oxide particles in the size of 10–40 nm are well dispersed in the slit pores stacked by rods of Pal. Most of the Cu–Mn oxides on Pal are with spinel structure, where Cu^{2+} ions occupy the tetrahedral sites and Mn^{3+} ions occupy the octahedral sites. The Pal-supported Cu–Mn oxides achieves 90% CO_2 generation at 207-258 °C, and displays better catalytic performance than solely supported catalyst. The presence of Cu obviously improves the reducibility of composite and the adsorption of HCHO, resulting in the acceleration of HCHO oxidation. The water resistance of composite catalyst also enhances with the increase of Cu content. Based on all these benefits, the catalytic performance of Cu–Mn oxides on Pal can be optimized with an increase of Cu level.

1. Introduction

The industrial discharge of high-concentration volatile organic compound (VOC) has aroused wide public concern, as they are hazardous to human health and trigger serious environmental problems including photochemical oxidants and ground level ozone (Yue et al., 2017). Some stringent professional standards have been legislated to restrict the discharge of industrial VOC (Sui et al., 2016; Zheng et al., 2017). Thus, the development of various physic-chemical technologies for the removal of VOC, e.g., adsorption (Kamravaei et al., 2017), photocatalysis (Lyu et al., 2017), and catalytic oxidation (Lu et al., 2016; Zhu et al., 2017), becomes an active area of research.

Catalytic oxidation is regarded as the most effective approach for the elimination of VOC using supported precious metals (e.g., Pt, Pd, Ag, and Au) or transition metal oxides (e.g., MnO_x, Fe_2O_3 and Co_3O_4) as catalysts (Zhang et al., 2016b). Compared to precious metals, transition metal oxides have the advantages of low cost, considerable reducibility and superior resistance to chloride and sulfur poisoning (Kamal et al., 2016). Currently, the recombination of two or more transition metal oxides is a novel strategy to improve the catalytic performance (Yang et al., 2015; Liu et al., 2016), owing to the synergetic effect derived from fast electron transfer between the coupled oxides. Recently, mixed Cu–Mn composite has drawn great attention. It has been reported that the mixed Cu–Mn oxides completely degraded toluene at approximately 220 °C, whose activity was comparable to that of Pd catalyst (Li et al., 2004). The finding that the formation of spinel phase is responsible for the high activity of Cu–Mn oxides exerts a significant impact on the further development of binary oxide catalyst (Vu et al., 2009; Aguilera et al., 2011). This allows the generation of structural defects and oxygen mobility through the redox couple $Mn^{4+} + Cu^{+} \leftrightarrow$

* Correspondence to: liangxl@gig.ac.cn (X. L. Liang)
** Corresponding author: cdxman@hfut.edu.cn (D. Chen).
E-mail addresses: liangxl@gig.ac.cn (X. Liang), cdxman@hfut.edu.cn (D. Chen).

https://doi.org/10.1016/j.clay.2018.04.032
Received 17 March 2018; Received in revised form 23 April 2018; Accepted 23 April 2018
0169-1317/ Crown Copyright © 2018 Published by Elsevier B.V. All rights reserved.

Table 1
The levels of Cu and Mn and BET specific surface area (SSA) of Cu−Mn oxides supported on Pal and their catalytic activity characterized by the temperature at 50% and 90% of HCHO oxidation.

Sample	[a]Cu content (wt%)	[b]Mn content (wt%)	[c]Cu/Mn	[d]SSA/$m^2\,g^{-1}$	[e]T50/°C	[f]T90/°C	[g]T50/°C	[h]TOF/s^{-1}
Pal-400	0	0	N/A	201	N/A	N/A	N/A	N/A
0Cu5Mn	0	4.4	0	221	236	265	247	1.3×10^{-4}
1Cu5Mn	0.9	4.5	0.18	208	232	258	240	1.5×10^{-4}
2.5Cu5Mn	2.4	4.5	0.45	211	214	243	214	2.3×10^{-4}
5Cu5Mn	4.8	4.5	0.92	216	201	221	197	4.1×10^{-4}
10Cu5Mn	8.7	4.2	1.8	205	185	207	181	6.3×10^{-4}
10Cu0Mn	9.7	0	N/A	214	241	276	N/A	8.0×10^{-5}
0Cu10Mn	0	10.3	0	225	231	248	N/A	7.0×10^{-5}

[a] The weight percentage of Cu on Pal determined by FAAS.
[b] The weight percentage of Mn on Pal determined by FAAS.
[c] The atomic ration of Cu/Mn level.
[d] SSA: specific surface area obtained by BET method.
[e] The temperature of 50% CO_2 generation rate at the absence of H_2O.
[f] The temperature of 90% CO_2 generation rate at the absence of H_2O.
[g] The temperature of 50% CO_2 under 5% H_2O.
[h] The turnover frequency at 200 °C defined as average number of CO_2 catalyzed by each Cu and Mn atom per second.

Mn^{3+} + Cu^{2+}, which facilitates the reactivation of catalyst (Aguilera et al., 2011). However, the "mixture effects", which are still largely unknown, are difficult to distinguish between Cu and Mn, especially in terms of the relative role in catalytic reaction and the effect on catalytic activity of binary oxides.

The catalytic oxidation of industrial VOC is generally carried out in 150-400 °C, which requires the active components well dispersed to avoid sintering. As is well known, supports not only improve the distribution of active components, but also favor the activity through the interaction with loading species. To date, a variety of supports such as Al_2O_3, TiO_2, ZrO_2, zeolites and carbon materials have been developed for mixed Cu−Mn oxide catalysts (Li et al., 2006; Doggali et al., 2012; Fan et al., 2014). Conventional supports still have some disadvantages, e.g., intricate synthetic procedures or costly ingredients, so that the exploration of less expensive but more easily available supports remains a challenge. The concern of natural clay minerals (e.g., halloysite, palygorskite, montmorillonite, and sepiolite) as supports attracts great research interest (He et al., 2011; Suarez et al., 2011; Carrillo and Carriazo, 2015; Tomul, 2016; Ouyang et al., 2018). For example, Palygorskite (Pal) owning nanorod-like morphology is a natural clay mineral with the general chemical formula of $Mg_5Si_8O_{20}(OH)_2(OH_2)_4{\cdot}4H_2O$ which has considerable substitution of magnesium by aluminum or iron. The abundant resource, large surface area (> 200 $m^2\,g^{-1}$), high thermal and chemical stability, plentiful nanopores, and efficient solid acid of Pal endow it with great potential to be catalyst support (He et al., 2013; Zhang et al., 2016a). Pal has been utilized as support for Pd−Cu and Fe−Ni oxides, and displayed efficient performance in CO oxidation and benzene decomposition (Liu et al., 2013; Wang et al., 2016). The high surface area results in the uniform dispersion of active components, while the meso- and macropores topology and strong solid acidic properties benefits the interaction and mass transfer of reactants. But in most studies, the microstructure of metal oxides on Pal and its effect on the catalytic activity are not explicit, ascribed to the superior dispersion.

To realize the aforementioned challenging issues, we chose Pal as a support of Cu−Mn oxides for the oxidation of formaldehyde (HCHO), which is a typical VOC as well as an important industrial reagent in building and furnishing materials (Prado et al., 2008). As we anticipated, the Pal-supported Cu−Mn oxides showed high catalytic activity and CO_2 selectivity. Through characterization and catalytic test, the following three aspects were studied with emphasis: i) the dispersion and microstructure of Cu−Mn oxides; ii) the effects of Cu and Mn on physico-chemical properties and catalytic performance; iii) the relative role of Cu and Mn in catalyzing HCHO oxidation.

2. Experimental

2.1. Synthesis of catalysts

Raw Pal sample derived from Mingguang, Anhui Province, China, was purified with sedimentation, acid wash, and sieving (mesh width 74 μm), and then labeled as Pal. The chemical composition (wt%) of Pal is shown in Text S1. The Pal suppported Cu−Mn oxide catalysts were prepared by an impregnation method. The prepared samples were denoted as 0Cu5Mn, 1Cu5Mn, 2.5Cu5Mn, 5Cu5Mn, 10Cu5Mn, 10Cu0Mn, and 0Cu10Mn, where the number in denotations correlates to the amount of Mn or Cu (wt% of Pal mass). To prepare 5Cu5Mn, 4 mL of Cu $(NO_3)_2$ solution (2.0 mol L^{-1}) and 4 mL of $Mn(NO_3)_2$ solution (2.0 mol L^{-1}) were sequentially introduced into 50 mL of Pal dispersion (200 g L^{-1}) under vigrous stirring. Then 32 mL of ammonia solution (1.5 mol L^{-1}) was added dropwise into above solution and the obtained Pal dispersion was stirred vigorously at 80 °C to evaporate solvent. Finally, the precusor was calcined at 400 °C in a muffle finance for 2 h. For comparison, the unsupported Cu−Mn oxides (Cu:Mn = 1:1 and 1:2) were synthesized by the similar procedure without the addition of Pal and was labled as $Cu_{1.5}Mn_{1.5}O_x$ and $CuMn_2O_x$, respectively. The Pal was also calcined at 400 °C and referred as Pal-400. The contents of Cu and Mn in the as-prepared catalysts are listed in Table 1, which are close to the predetermined levels.

2.2. Characterization

The contents of Cu and Mn were determined by PerkinElmer AAnalyst 400 Flame Atomic Absorption Spectrometry after the complete dissolution of Cu−Mn oxides by a mixture of nitric acid and hydrochloric acid. The X-ray diffraction (XRD) patterns were recorded between 5° and 70° (2θ) at a step of 2° min^{-1} on a Bruker D8 advance diffractometer with Cu Kα radiation (40 kV and 40 mA). The specific surface area (SSA) was calculated by a multipoint Brunauer-Emmett-Teller method on the basis of N_2 adsorption-desorption isotherms in the relative pressure (P/P_0) of 0.08–0.20. Before each test the samples were degassed at 150 °C for 12 h to remove adsorbed species. The scanning electron microscope (SEM) images were observed by a Hitachi SU8010. The transmission electron microscope (TEM) images were obtained using JEOL JEM-2100F operated at 200 kV. The element composition was characterized by an energy dispersive spectrometer attached to TEM. The samples was prepared by dropping ethanol solution after sonication onto carbon coated 400 mesh nickel grids which could avoid the perturbation Cu grids might cause. Hydrogen temperature programmed reduction (H_2-TPR) was conducted in the range of 30-900 °C

Download English Version:

https://daneshyari.com/en/article/8045799

Download Persian Version:

https://daneshyari.com/article/8045799

Daneshyari.com