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Copper–manganese oxide catalysts supported on alumina: Physicochemical features and catalytic performances in the aerobic oxidation of benzyl alcohol

Qinghu Tang[a,b,*], Xiaonan Gong[a], Peizheng Zhao[a], Yuanting Chen[b], Yanhui Yang[b,**]

[a] School of Chemistry and Environmental Science, Key Laboratory of Green Chemical Media and Reactions, Ministry of Education, Henan Normal University, Xinxiang 453007, China
[b] School of Chemical and Biomedical Engineering, Nanyang Technological University, Singapore 637459, Singapore

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ABSTRACT

We report the facile synthesis of alumina supported copper–manganese mixed oxide catalysts by a homogeneous deposition–precipitation method and the catalytic applications of these catalysts in the oxidation of benzyl alcohol using molecular oxygen. Benzyl alcohol conversion of ca. 90.9% was achieved with benzaldehyde as the main product. The catalyst can be recycled consecutively up to seven runs without appreciable loss of its activity and selectivity. Characterizations with X-ray diffraction, transmission electron microscopy, Raman, X-ray absorption spectroscopy, and hydrogen temperature-programmed reduction suggested the formation of a mixed oxide ($Mn_{1.5}Cu_{1.5}O_4$) microcrystalline phase after adding copper to the manganese supported on alumina. Such formation would account for the high catalytic performance. Calcination under high temperature decomposed this mixed oxide phase, resulting in a poor catalytic activity.

1. Introduction

Selective oxidation of alcohols to carbonyl compounds over heterogeneous catalysts using molecular oxygen (aerobic oxidation) has attracted significant attention from the viewpoint of establishing green and sustainable chemical processes [1]. Many studies have been focused on the aerobic oxidation of alcohols using supported noble metal catalysts, e.g., Ru-, Pd- and Au-based catalysts [2]. Nevertheless, researchers still need to explore the use of various inexpensive transition metals, such as Mn-, Ni- and Cu-containing catalysts, though their catalytic activity is dramatically poorer than those of precious metals. In fact, less expensive metals offer a cost-effective alternative to the noble metal catalysts, and low catalytic activity may give more insight into the reaction mechanism [3–14].

A synthetic manganese oxide molecular sieve with channel structures was reported as a superior catalyst for the aerobic oxidation of alcohols in liquid-phase in the presence of molecular oxygen as the oxidant [3–6]. Ni–Al hydrotalcite-like materials and nickel containing magnesium–aluminum hydrotalcite type anionic clays were also effective in catalyzing the aerobic oxidation of alcohols [7,8]. Solvent-free oxidation of alcohols with molecular oxygen was successfully performed over Cu and Mn containing hydrotalcite-like anionic clays [9]. Su et al. demonstrated that manganese oxides were highly efficient in the solvent-free oxidation of benzyl alcohol under microwave irradiation [10]. Amorphous MnO_x and Mn–Ce–O were found to exhibit high catalytic activities in the aerobic oxidation of benzolic alcohols using molecular oxygen [11,12]. Recently, a remarkable improvement of activity in the aerobic oxidation of aromatic alcohols has been observed after modifying the supported manganese oxide catalysts with potassium cations [13,14].

Craciun et al. [15] and Wöllner et al. [16] found that the mixtures of manganese oxide and other metal oxides, in particular copper oxide, exhibited a higher activity than mono-component catalysts in CH_4 oxidation. Adding a small amount of copper notably improved the catalytic performances of a manganese-based catalyst in ethanol and propane combustion [17]. Copper–manganese mixed oxide has been investigated as an efficient catalyst in the oxidation of carbon monoxide [18–22], ammonia, and other gaseous species [14]. Manganese and copper were also reported as concordant partners in the oxidation of *p*-cresol [23,24] and toluene [25].

In the present work, mixed copper and manganese oxides supported on alumina ($CuMn/Al_2O_3$) were synthesized and their catalytic properties in the aerobic oxidation of benzyl alcohol were examined. The catalytic results were analyzed with respect

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* Corresponding author at: School of Chemistry and Environmental Science, Key Laboratory of Green Chemical Media and Reactions, Ministry of Education, Henan Normal University, Xinxiang 453007, China. Tel.: +86 373 3326335; fax: +86 373 3326336.
** Corresponding author. School of Chemical and Biomedical Engineering, Nanyang Technological University, 62 Nanyang Drive, N1.2-B1-18, Singapore 637459, Singapore. Tel.: +65 6316 8940; fax: +65 6794 7553.
E-mail addresses: qinghutang@sina.com.cn (Q. Tang), yhyang@ntu.edu.sg (Y. Yang).

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to the state and structure of supported manganese and copper species. Complementary characterization techniques, such as X-ray diffraction (XRD), N_2 physisorption, Raman, transmission electron microscopy (TEM), X-ray absorption spectroscopy (XAS), and hydrogen temperature-programmed reduction (H_2-TPR) were employed to reveal the physicochemical features of these catalysts.

2. Experimental

2.1. Catalyst synthesis

The γ-Al_2O_3 support with a specific surface area of 224 $m^2\,g^{-1}$ was prepared by precipitating $Al(NO_3)_3 \cdot 9H_2O$ (Sigma–Aldrich, $\geq$98%) in $NH_3 \cdot H_2O$ (Sigma–Aldrich, $\geq$25% NH_3 in water) at pH 9.0 followed by calcination at 773 K in air for 3 h. The $CuMn/Al_2O_3$ catalysts were prepared by a facile homogeneous deposition–precipitation method. Typically, 1.0 g of calcined alumina was added into a $Mn(NO_3)_2$ (Fluka, $\geq$97.0%) and Cu $(NO_3)_2$ (Sigma–Aldrich, 99%) aqueous solution (50 mL), followed by adding NaOH (0.1 mol L^{-1}) dropwise under vigorous stirring at room temperature until the pH became 10.0. The resulting slurry was aged at room temperature for 24 h, filtered and washed with deionized water until neutral pH. The as-prepared catalysts were dried at 383 K overnight followed by calcination at different temperatures in air for 3 h. The total metal content was set as ca. 1.82 mmol g^{-1} for all the samples.

2.2. Characterizations

Powder XRD patterns were recorded on a Bruker Advance 8 X-ray diffractometer equipped with a rotating anode using Cu Kα radiation (λ = 0.154 nm, 40 kV, 40 mA). N_2 physisorption isotherms were measured at 77 K on a static volumetric Autosorb 6B (Quanta Chrome). Prior to the measurement, samples were degassed at 423 K to a residual pressure below 10^{-4} Torr. The specific surface area was calculated by the Brunauer–Emmett–Teller (BET) method. TEM analysis was conducted on a JEM-1400 (JEOL) operated at an acceleration voltage of 120 kV. The samples were suspended in ethanol and dried on holey carbon-coated Cu grids. Manganese and copper contents were analyzed using a Dualview Optima 5300 DV ICP-OES system after completely dissolving the sample in a mixture of nitric acid and hydrochloric acid.

Raman spectra were recorded on a Renishaw in Via Raman Microscope system using a 514.5 nm laser as excitation source. A laser output of 30 mW was used and the maximum incident power at the sample was approximately 6 mW. The Mn K-edge and Cu K-edge X-ray absorption spectra were measured at the X-ray Demonstration and Development beam line of the Singapore Synchrotron Light Source (SSLS) in a transmission mode under ambient conditions [26].

The reducibility of $MnCu/Al_2O_3$ was examined by H_2-TPR on Autosorb-1C (Quanta Chrome) equipped with a thermal conductivity detector (TCD). Prior to the H_2-TPR, 100 mg of powder sample was purged in ultra zero grade air at 383 K for 1 h, and then cooled to room temperature. The gas flow was switched to 5 vol.% hydrogen in argon balance, and the base line was monitored until it became stable. The sample cell was heated at a ramping rate of 8 K min^{-1} from 373 to 1073 K.

2.3. Catalytic reaction

The aerobic oxidation of benzyl alcohol was carried out in a bath-type reactor operated under atmospheric conditions. Three hundred milligrams of catalyst was added to a 50 mL glass flask pre-charged with 2 mmol benzyl alcohol and 10 mL toluene. The mixture was heated to 373 K under vigorous magnetic stirring. Oxygen flow at a flow rate of 10 $cm^3\,min^{-1}$ was bubbled into the mixture to start the reaction. After the reaction, the liquid samples were analyzed by GC after adding dodecane as the internal standard (see Ref. [13] for detailed information). The spent $CuMn/Al_2O_3$ catalyst was washed with acetone, 0.1 mol L^{-1} NaOH solution and deionized water. After drying at 383 K for 3 h, the catalyst was reused in the subsequent reaction runs.

3. Results and discussion

3.1. Catalytic performance of $CuMn/Al_2O_3$ catalysts

The catalytic results of $CuMn/Al_2O_3$ catalysts with different Cu/Mn molar ratios (the total metal loading is constant) are shown in Table 1. Benzaldehyde is the main product, with a negligible amount of benzoic acid as byproduct. Alumina support is inactive in this particular reaction. Mn/Al_2O_3 shows a high catalytic activity with the benzyl alcohol conversion of ca. 65.6%. Adding copper to Mn/Al_2O_3 remarkably improves the catalytic activity and maintains the high selectivity towards benzaldehyde, though the amount of Mn is reduced. There is a great possibility that Cu/Al_2O_3 may also show catalytic activity in the oxidation of benzyl alcohol, because Choudhary and co-workers reported the high activity of Cu-containing hydrotalcite-like anionic clays in the oxidation of alcohols with molecular oxygen under solvent-free conditions [9]. Nevertheless, the Cu/Al_2O_3 catalyst only shows the benzyl alcohol conversion of ca. 2.2% in this study. Thus, adding copper to the supported manganese oxide results in a particularly active phase for the aerobic oxidation of alcohols, due to the synergetic effect between copper and manganese. Similar results have also been reported by Hutchings et al. [21,22] and Morales et al. [17,27] in the oxidation of CO, ethyl acetate, and ethanol. The benzyl alcohol conversion increases with increasing the Cu/Mn ratio. $Cu1Mn4/Al_2O_3$ shows the best benzyl alcohol conversion of ca. 90.9%. Further increasing the Cu/Mn ratio, however, results in the poor catalytic activity, e.g., only ca. 45.9% of benzyl alcohol is converted over Cu_1Mn_1/Al_2O_3 due to the coverage of active sites by excess amounts of copper.

Calcination in air may play a vital role in forming the dispersed MnO_x and CuO_x species for supported Cu–Mn catalysts [27]. In this study, calcination temperature was found to be a significant factor for controlling the catalytic properties of $CuMn/Al_2O_3$ catalysts, as summarized in Table 2. The best catalyst $Cu1Mn4/Al_2O_3$ was selected as a representative example. The catalyst dried at 383 K without calcination exhibits the highest benzyl alcohol conversion. There is no noticeable change for the catalytic activity when the calcination temperature is below 573 K; further increasing the calcination temperature leads to the gradual loss of the catalytic activity. These results suggest that low-temperature calcination gives rise to the formation of highly active Cu–Mn oxide species

Table 1

Aerobic oxidation of benzyl alcohol over $MnCu/Al_2O_3$-383K catalysts[a].

Catalyst	Mn:Cu atomic ratio	Conversion (%)	Aldehyde selectivity (%)
Al_2O_3	–	<1.0	97
Cu/Al_2O_3[b]	–	2.2	>99
Mn/Al_2O_3	–	65.6	>99
$Cu1Mn20/Al_2O_3$	1:20	73.9	>99
$Cu1Mn10/Al_2O_3$	1:10	81.7	>99
$Cu1Mn4/Al_2O_3$	1:4	90.9	>99
$Cu1Mn2/Al_2O_3$	1:2	71.2	>99
$Cu1Mn1/Al_2O_3$	1:1	45.9	>99

[a] *Conditions*: catalyst = 0.3 g, *T* = 373 K, benzyl alcohol = 2 mmol, toluene = 10 mL, O_2 flow rate = 10 $cm^3\,min^{-1}$, reaction time = 4 h, C-balance = 97–103%.

[b] Copper content is the same as that of $Cu1Mn4/Al_2O_3$ sample.