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Methanol dehydrogenation to methyl formate catalyzed by SiO_2-, hydroxyapatite-, and MgO-supported copper catalysts and reaction kinetics

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ABSTRACT

Catalytic dehydrogenation of methanol to methyl formate over SiO_2-, hydroxyapatite (HAP)-, and MgO-supported copper catalysts was investigated. Metallic copper (Cu^0) was the active site for the methanol dehydrogenation to methyl formate. Cu/SiO_2 catalyst with low basicity and weak-strength basic site effectively catalyzed the methanol dehydrogenation to methyl formate. Cu/HAP and Cu/MgO catalysts with high basicities and strong-strength basic sites caused the degradation of the resultant methyl formate to CO and H_2. Over $Cu(5)/SiO_2$ catalyst, the reaction activation energies for methanol dehydrogenation to methyl formate and methyl formate degradation to CO and H_2 were 58.3 and 91.1 kJ mol^{-1}, respectively.

Introduction

Methyl formate is a valuable chemical widely used as an antiseptic, solvent, gasoline additive, and versatile chemical intermediate for the synthesis of dimethyl formamide, acetic acid, and ethylene glycol [1–6]. Methyl formate can be produced by the processes, such as esterification of methanol with formic acid, carbonylation of methanol, oxidative dehydrogenation of methanol, and dehydrogenation of methanol [1]. The esterification of methanol with formic acid to methyl formate was conventionally catalyzed by corrosive mineral acids. The carbonylation of methanol to methyl formate was carried out using alkaline metal methoxide as the catalyst with 2–7 MPa of CO. The oxidative dehydrogenation of methanol to methyl formate was catalyzed by MoO_3- or WO_3-containing catalyst. However, the production capacity of methyl formate was only 0.06 g $g_{cat}{}^{-1}$ h^{-1} and the resultant H_2 could be oxidized to H_2O. As compared with the above mentioned routes, synthesis of methyl formate *via* the methanol dehydrogenation route appears to be technically feasible.

Direct dehydrogenation of methanol to methyl formate has attracted great attention because it is an economically and environmentally friendly alternative to the conventionally commercial processes [3–7]. In the methanol dehydrogenation reaction, methyl formate is produced as the main product, accompanied with the formation of carbon monoxide (CO) and H_2 as the by-products. Methanol is firstly dehydrogenated to intermediate formaldehyde, which could easily react with methanol to form methyl formate [6,8,9]. The corresponding reactions are described as Eqs. (1) and (2).

$$CH_3OH \rightarrow CH_2O + H_2 \tag{1}$$

$$CH_2O + CH_3OH \rightarrow HCOOCH_3 + H_2 \tag{2}$$

By combining Eqs. (1) and (2), Eq. (3) is obtained as follows.

$$2CH_3OH \rightarrow HCOOCH_3 + 2H_2 \tag{3}$$

At a high reaction temperature, the selectivity of methyl formate was limited by the consecutive degradation to CO and H_2 [6,9]. The corresponding reaction is shown as equation (4).

$$HCOOCH_3 \rightarrow 2CO + 2H_2 \tag{4}$$

Copper-based catalysts, such as Cu/Cr_2O_3 [3,8,9], Cu/SiO_2 [6,10], Cu-exchanged clays [11], and $Cu/ZnO/Al_2O_3$ [12], have been investigated for the methanol dehydrogenation to methyl formate. According to the researches [10,13,14], Cu^0 species were found to be the sole active sites for alcohol (methanol and ethanol) dehydrogenation to their esters. In our previous work, the catalytic

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activities of the catalysts, such as Cu/Al_2O_3, Cu/MCM-41, Cu/H-ZSM-5, and Cu/H-β, with high acidities for ethanol and methanol dehydrogenation have been investigated [15–17]. Although these catalysts exhibited high catalytic activities for the conversion of ethanol and methanol, low selectivities of ethyl acetate and methyl formate were obtained. The product distribution indicated that the acid sites present in these catalysts caused the intermolecular dehydration of ethanol and methanol to their ethers. These results revealed that the catalysts with high acidities were not suitable for the dehydrogenation of ethanol and methanol to ethyl acetate and methyl formate, respectively. The effect of surface acidities of supported copper catalysts on alcohol dehydrogenation was investigated. However, the effect of surface basicities of supported copper catalysts on alcohol dehydrogenation has rarely been investigated.

In the present work, the catalytic activities of the SiO_2-, hydroxyapatite (HAP)-, and MgO-supported copper catalysts with different basicities for the methanol dehydrogenation to methyl formate were investigated in a fixed bed reactor. The physicochemical properties of these catalysts were characterized by XRD, XPS, BET, H_2-TPR, and CO_2- and NH_3-TPD techniques. A power function-type reaction kinetic model was used to evaluate the reaction kinetics of both methanol dehydrogenation and methyl formate degradation reactions.

Experimental

Chemicals

Methanol, methyl formate, copper nitrate trihydrate ($Cu(NO_3)_2{\cdot}3H_2O$), magnesia (MgO), calcium nitrate tetrahydrate ($Ca(NO_3)_2{\cdot}4H_2O$), phosphoric acid (H_3PO_4, 85%), and ammonia solution ($NH_3{\cdot}H_2O$, 25%) were of reagent grade and were purchased from Sinopharm Chemical Reagent Co., Ltd. Silica aerogel (SiO_2) was purchased from Jiangsu Haoneng Chemical Co., Ltd.

Preparation of catalyst

The support, hydroxyapatite (HAP), was prepared by the hydrothermal method described as follows. An aqueous solution of $Ca(NO_3)_2{\cdot}4H_2O$ (1 mol L^{-1}) and H_3PO_4 (0.6 mol L^{-1}) was added into a three-necked flask in a water bath at 40 °C. An ammonia solution (25%) was added dropwise to adjust the pH value of the reaction solution to 10. After stirring at 40 °C. for 4 h, the resultant suspension was transferred into a Teflon-lined autoclave and autoclaved at 100 °C. for 10 h. The resultant powder was washed with deionized water until the conductivity of the filtrate was less than 2 mS m^{-1} and then dried at 120 °C. overnight.

Copper-based catalysts were prepared by the incipient wetness impregnation method. Thirty grams of supports (SiO_2, HAP, and MgO) were impregnated with a given amount of copper nitrate aqueous solution at room temperature. After impregnation, the samples were dried at 120 °C. overnight and then calcined at 550 °C. for 4 h. The weight percentages of metallic Cu in the as-prepared catalysts were 5%, 10% and 20%, respectively. The catalysts were pressed at 12 MPa and then crushed into particles with the particles sizes ranging from 0.45 to 0.8 mm. The as-prepared catalysts were denoted by Cu(x)/SiO_2, Cu(x)/HAP, and Cu(x)/MgO, where x represented the metallic Cu loading (%).

Characterization of catalyst

Powder XRD was used to examine the bulk chemical structures of the calcined and reduced catalysts. The XRD data of the calcined and reduced catalysts were recorded on a diffractometer (D8 super speed Bruke-AEX Company) using Cu Kα radiation (λ = 1.54056 Å) with Ni filter. The crystallite sizes of Cu^0 (1 1 1) in the reduced catalysts were calculated by using Scherrer's equation, $D = K\lambda/(B\cos\theta)$, where K was taken as 0.89 and B was the full width of the diffraction line at half of the maximum intensity. The results are listed in Table 1.

X-ray photoelectron spectra (XPS) of the reduced Cu(20)/MgO catalyst were recorded on an XSAM800 spectrometer (Kratos Company) using Al Kα radiation (1486.6 eV). The binding energies were calculated with respect to C1s peak of contaminated carbon at 284.6 eV.

The specific surface areas of the reduced catalysts were measured by the N_2 adsorption/desorption method at −196 °C. using a NOVA 2000e physical adsorption apparatus and the BET analysis method. Prior to the measurement, the samples were degassed at 300 °C. in a N_2 flow for 0.5 h to remove the physically adsorbed water.

The reduction behaviors of the catalysts were investigated by TPR technique using 0.1 g of calcined catalysts with a mixed H_2/N_2 flow (5:95, v/v) of 30 mL min^{-1}. The samples were heated from 50 to 480 °C. at a heating rate of 10 °C min^{-1}.

The surface basicities and acidities of the reduced catalysts were determined by CO_2- and NH_3-TPD techniques in a fixed bed continuous flow micro-reactor at atmospheric pressure. For the basicity measurement, the reduced catalysts (0.1 g) were CO_2-saturated in a CO_2 stream for 0.5 h. After purging with helium (30 mL min^{-1}) at 100 °C. for 0.5 h to remove the physically adsorbed CO_2, the samples were heated at a linear heating rate of 10 °C min^{-1} up to 700 °C. For the acidity measurement, the reduced catalysts (0.1 g) were NH_3-saturated in a NH_3 stream for 0.5 h. After purging with helium (30 mL min^{-1}) at 100 °C. for 0.5 h to remove the physically adsorbed NH_3, the samples were heated at a linear heating rate of 10 °C min^{-1} up to 700 °C.

Table 1
Physicochemical properties of copper-based catalysts.

Catalysts	Specific surface areas ($m^2\,g^{-1}$)	Crystallite sizes of Cu^0 (1 1 1) (nm)	Base site distributions (μmol CO_2/g_{cat})			Total basicities (μmol CO_2/g_{cat})	Total acidities (μmol NH_3/g_{cat})	H_2 consumptions[a] (mmol H_2/g_{cat})	Conversions of CuO[a] (%)
			Weak	Medium	Strong				
Cu(5)/SiO_2	115.4	29.9	163.6	–	–	163.6	500.7	0.47	60.2
Cu(10)/SiO_2	113.7	32.6	140.1	–	–	140.1	461.3	0.94	60.2
Cu(20)/SiO_2	109.4	35.2	115.5	–	–	115.5	423.3	1.92	61.4
Cu(5)/HAP	55.2	27.7	322.2	–	143.7	465.9	–	0.51	65.3
Cu(10)/HAP	47.7	30.3	132.5	–	391.7	524.2	–	1.11	71.0
Cu(20)/HAP	43.1	34.6	91.9	–	575.8	667.7	–	2.36	75.5
Cu(5)/MgO	40.7	–	79.8	1486.1	–	1565.9	–	0.43	55.0
Cu(10)/MgO	36.1	–	29.3	1368.7	–	1398.0	–	0.89	56.9
Cu(20)/MgO	26.2	–	12.3	1173.6	–	1185.9	–	1.78	57.0

[a] The H_2 consumptions of the calcined copper-based catalysts were calculated from the TPR curves. And the conversion of CuO was calculated by assuming conversion of CuO to metallic copper.