Methyl formate synthesis from methanol on titania supported copper catalyst under UV irradiation at ambient condition: Performance and mechanism

Jie Liu [a], Chenhui Han [a], Xuzhuang Yang [a,*], Guanjun Gao [a], Quanquan Shi [b], Min Tong [a], Xiaoyuan Liang [a], Changfu Li [a]

[a] School of Chemistry and Chemical Engineering, Inner Mongolia University, Hohhot, Inner Mongolia 010021, PR China
[b] State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, PR China

ABSTRACT

Selective oxidation of methanol to methyl formate (MF) with high MF formation rate and simple by-products at ambient conditions is a challenging process. Herein, we report the methyl formate synthesis from methanol on a titania supported copper catalyst in a flow reactor at 15–45 °C under UV irradiation. The MF formation rate reaches 56.4 mmol $g^{-1}\,h^{-1}$. Carbon dioxide is the only by-product below 30 °C, and very small amount of dimethoxymethane besides carbon dioxide can be detected at 45 °C. CuO on titania in the as-prepared catalyst is reduced to Cu to form an Ohmic contact between Cu and titania during the reaction under UV irradiation, which facilitates the photo-excited electron transfer from the conduction band of titania to Cu and reduces the recombination of the photo-excited electron–hole pairs. The negative charge on the Cu surfaces promotes the dissociation of oxygen. The coordinated methoxy resulted from the dissociative chemisorption of methanol on the surface of titania is oxidized by the photo-generated holes to form coordinated surface formaldehyde. The oxygen dissociation and the oxidation of coordinated methoxy are parallel reactions, and both of them are rate-controlled by light intensity. This study may contribute to design new photocatalytic systems and provide an applicable green route to MF synthesis from methanol.

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1. Introduction

The replacement of the out-of-date processes by the new green routes in the chemical industry is essential to reduce the environmental impact and achieve the sustainability of resources [1,2]. Methyl formate (MF) is an important intermediate for producing formic acid, formamides, acetic acid and ethylene glycol [3–6], traditionally produced by the dehydrogenation of methanol under the thermal condition [3–10]. Such processes are usually performed at elevated pressures and temperatures, leading to energy waste, multi-by-products and low MF selectivity (S) [4,5,7–9,11], and thus increasing the production cost and the environmental impact. The new green routes working at mild conditions have attracted much attention in recent years [12–15].

Wittstock et al. [12] have reported that methanol can be oxidized to MF on a nanoporous gold catalyst prepared by dealloying Ag from an Au–Ag alloy, with ca. 100% S at ca. 10% methanol con-

version (C) at 20 °C. This work shed new light on the green MF synthesis although the investment on the catalyst might be spectacular. Liu et al. [16] reported a photocatalytic route to the MF production on MoO_3/TiO_2 and TiO_2 as early as 1985. Kominami et al. [15] studied the same reaction on an anatase-type TiO_2 (ST-01) in 2010. However, the MF formation rate (Fr) reported by the two groups is far below that on the nanoporous gold catalyst at ambient condition, especially, a large amount of by-products such as dimethoxymethane (DMM), dimethylether (DME), formaldehyde, carbon dioxide and/or carbon monoxide being formed at elevated temperatures. To raise C at high S has become a hot issue in this area. In our previous work [13], we have prepared Au–Ag alloy nanoparticles supported on titania for MF synthesis from methanol at 15–45 °C under UV irradiation, obtaining comparable Fr with that on the nanoporous gold catalyst. The only by-product is CO_2. The Au–Ag alloy nanoparticles play important roles in the charge separation and the oxygen dissociation.

Copper has the similar outer electronic configuration as that of Au and Ag, but it is far cheaper than gold and silver. In particular, the work function of Au ($\varphi_{Au} = 5.420$ eV) is larger than that of

* Corresponding author. Tel.: +86 471 4992982; fax: +86 471 4992981.
E-mail address: xzyang2007@yahoo.com (X. Yang).

titania ($\varphi_{Titania}$ = 4.70 eV) [17], the Schottky barriers being formed at the interface between Au and titania. The photo-excited electrons in the conduction band of titania have to overcome the energy barrier to reach Au. But the work function of Cu (φ_{Cu} = 4.60 eV [18,19]) is slightly smaller than that of titania, which can result in an Ohmic contact at the interface between Cu and titania. And thus the electrical resistance at the interface between Cu and titania must be smaller than that in the conduction band of titania. The photo-excited electrons in the conduction band of titania may be, accordingly, more readily to flow to the Cu sites. As a result, it is very expected and of great significance to replace Au and Ag by Cu. However, Cu nanoparticles impossibly exist in air or even in the presence of trace oxygen, and they are readily oxidized to Cu_2O or CuO [20,21]. Copper oxides Cu_2O and CuO are p-type semiconductors, having narrow band gaps of 2.0 eV [22–25] and 1.7 eV [25,26], respectively, and appropriate conduction band edges [25,27–29], and thus have been used for H_2 production [28,30–32], CO_2 reduction [33–38], organics degradation [39,40] or photosynthesis [41] by visible light irradiation in recent years. Metallic Cu nanoparticles can only be stabilized on special support such as graphene, and the localized surface plasmon resonance (LSPR) of the conduction electrons induced by incident visible light is responsible for the reaction [41]. Although copper oxides have been widely studied, they are unstable under irradiation because the redox potentials for reduction and oxidation of monovalent copper oxide lie within their band gaps [22,42,43], which hinders their application. Given that copper oxides supported on titania can be photo-reduced to metallic Cu under UV irradiation, the Ohmic contact between Cu and titania can be formed, which will facilitate the charge separation and oxygen dissociation on Cu nanoparticles during the selective oxidation of methanol to MF and thus be favorable to the reaction.

In the present study, we have prepared copper catalysts supported on titania by the reduction-deposition method in order to confirm our conjecture. The catalysts have been used for MF synthesis from methanol at 15–45 °C under UV irradiation. The *C*, *S*, *Fr*, and the impact of the light intensity, the initial methanol concentration and the initial oxygen concentration on the catalytic performance have been investigated. The transformation mechanism of the Cu species on the catalyst at different stages as well as the reaction mechanism has been proposed according to a series of characterization.

2. Experimental

2.1. Materials

P25(Degussa) was purchased from J & K Scientific. $NaBH_4$ and $Cu(NO_3)_2$ were purchased from Sinopharm Chemical Reagent Co. Ltd. All chemicals were used as received.

2.2. Catalyst preparation

Typically, titania (Degussa P25, BET surface area, 57 $m^2\,g^{-1}$) was ultrasonically dispersed in a 0.01 mol l^{-1} $Cu(NO_3)_2$ solution for 25 min followed by adding a $NaBH_4$ solution (Cu:$NaBH_4$ = 1:2.5, molar ratio) with vigorously stirring for 24 h. The solid recovered was dried at 50 °C in air after washing by deionized water and ethanol. The catalyst was labeled as Cu/TiO_2-x, where *x* denoted the Cu mass content. The catalyst calcined at 350 °C in air for 1 h as reference was labeled as Cu/TiO_2-xC.

2.3. Catalyst characterization

X-ray diffraction (XRD) measurements were performed using a PANalytical B.V. Empyrean diffractometer with a Cu K_α radiation

operated at 40 kV, 40 mA. The scanning range (2θ) was 10°–80°. The morphology of the samples was investigated by a FEI Tecnai S-Twin transmission electron microscopy (TEM). Light absorbance was measured by a UVIKON/XL UV–vis diffuse reflectance spectrometer (UV–vis) with a scanning range of 200–800 nm. The metal content was measured by the energy-dispersive spectrometry (EDS) using the Brucker-QUANTAX 200 microanalysis system equipped on a Hitachi S-4800 field emission scanning electron microscope (SEM). The temperature programmed reduction with hydrogen (H_2-TPR) was performed with a Micromeritics AutoChem 2910 analyzer. The gas mixture is 10% H_2 balanced with N_2 and the flow rate is 50 mL/min. The heating rate is 10 °C/min. 10 mg sample was loaded in the quartz tube for each run. The X-ray photoelectron spectra (XPS) of the catalysts were recorded by a Kratos Amicus spectrometer using an Al K_α (1486.6 eV) radiation source. The binding energy (BE) was adjusted by the C1s transition at 284.6 eV. The light intensity was measured by a UV Integrator (UV-BIKESU). The typical process was as following. Firstly, install the UV probe 4 mm under the quartz window used for the reaction, and fix the light source in a specific distance over the quartz window. Secondly, turn on the light and start timing. The light intensity was then obtained using the measured power accumulation divided by the area of the probe and the time of irradiation. The light intensity can be modulated by adjusting the distance between the light source and the quartz window.

2.4. Photocatalytic reaction

The photocatalytic activity of the catalyst was performed in a continuous flow aluminum alloy reactor with a rectangle quartz window on the top and a dividing wall-type heat exchanger connected to the back of the bottom of the reactor [13]. The dimension of the reactor can be seen in the supporting information (Fig. s1). Three pieces of rectangle glass which were used as the catalyst holders coated by the catalyst of 0.02 g on their top surfaces were installed in the bottom of the reactor, with a thermocouple fixed in touch with the middle catalyst holder. The dimension of each piece of the glass holders was 26 mm × 80 mm × 1 mm. The whole surface coated by catalyst can be irradiated by light. The cooling water flowed through the heat exchanger to maintain a constant temperature. A 500 W high pressure mercury lamp (CEL-LAM500) with a quartz cooling jacket, peaking at 365 nm without filter, was positioned 2 cm over the quartz window of the reactor. In this case, the light intensity is 18.6 mW/cm^2. A gas mixture containing 1–3 vol.% methanol and 0.17–20 vol.% O_2 balanced with N_2 was supplied at the flow rate of 50 ml/min into the reactor. The operation pressure was 1 atm. Oxygen and nitrogen in the mixture were measured by mass flowmeters. The reaction temperature was controlled at 15–45 °C. The products were qualified by a GC–MS and a LC–MS in batches and quantified online by a Shimadzu GC2014C equipped with a FID detector.

The methanol conversion was obtained by Eq. (1), assuming the volume flow rate was constant before and after the reaction due to the low reactant content in the feed gas.

$$C = \frac{\rho_{M0} - \rho_{M1}}{\rho_{M0}} \times 100\% \qquad (1)$$

where *C* is the methanol conversion, %; ρ_{M0} is the initial methanol content, mg L^{-1}; ρ_{M1} is the methanol content in the offgas after reaction, mg L^{-1}. The selectivity of methyl formate was calculated by the following Eq. (2)

$$S = \frac{2\rho_{MF}}{\rho_{M0} - \rho_{M1}} \times 100\% \qquad (2)$$

where *S* is the methyl formate selectivity, %; ρ_{MF} is the methyl formate content in the offgas after reaction, mg L^{-1}.