

Short Communication

Photocatalytic oxidation of methanol to methyl formate in liquid phase over supported silver catalysts



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ABSTRACT

The selective oxidation of methanol to methyl formate by oxygen in the liquid phase under UV irradiation was investigated on supported silver catalysts. The catalysts exhibited high performance in the formation of methyl formate. The silver nanoparticles on P25 promoted the reaction through removing the photoexcited electrons from the surface of titania to extend the hole–electron lifetime. The surface plasma resonance (SPR) of the silver nanoparticles on silica was responsible for the formation of methyl formate. UV light itself was slightly active to the formation of methyl formate.

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1. Introduction

Methyl formate (MF) is an important building block in organic chemistry for producing formic acid, formamides, acetic acid and ethylene glycol etc. [1–3] It is typically produced by carbonylation [4,5], dehydrogenation [1,6,7] or selective oxidation of methanol [2,3,8,9], or direct synthesis from syngas [10]. Kominami et al. [11] reported the pioneering work of photocatalytic oxidation of gaseous methanol to methyl formate on titania in 2010. Qin et al. [12] studied the photocatalytic reduction of CO₂ in methanol to methyl formate over the CuO–TiO₂ catalyst in 2011. Guo et al. [13] have observed the formation of methyl formate on TiO₂(110) under irradiation. Phillips et al. [14] have demonstrated two consecutive photo-oxidation steps leading to methyl formate from methanol. The photocatalytic process becomes a new route to the production of methyl formate from methanol.

Silver supported on titania has usually been used in pollutant degradation as an efficient photocatalyst [15–18]. The Schottky barriers at the interface between silver and titania [15,16,19] and/or the SPR of silver nanoparticles [20,21] have been reported to be responsible for the good photocatalytic performance. The Schottky barriers can remove the photoexcited electrons from the surface of titania to metallic silver and thus reduce the electron–hole recombination [15,16,19], and the SPR of silver nanoparticles can introduce a strong local electronic field in the vicinity of the nanoparticles [20–22], which is believed being capable of inducing some reactions. The Ag/SiO₂ has been reported to be active in oxidative dehydrogenation of methanol to formaldehyde [23,24] and partial oxidation of benzyl alcohol to benzaldehyde [25].

In addition, it has also been used as the photocatalyst for degradation of organic compounds and selective oxidation of benzyl alcohol to benzaldehyde [26], the SPR and the electron interband transition from 4d to 5sp of silver nanoparticles on silica resulting in the high photocatalytic activity. However, the catalyst of silver supported on titania or silica has seldom been studied for the photocatalytic oxidation of methanol to methyl formate.

In this study, supported silver catalysts were prepared by the colloid deposition method. The photocatalytic performances of the catalysts for selective oxidation of methanol to methyl formate were investigated under the irradiation of UV or visible light. The objectives of this study are to investigate the influences of silver nanoparticles, supports and wavelength of light on the photocatalytic activity of selective oxidation of methanol to methyl formate.

2. Experimental

Two grams of P25 or silica was dispersed in an as-prepared ice-cold sodium borohydride solution of 2×10^{-3} mol/l with stirring. A suitable amount of the ice-cold AgNO₃ solution of 5×10^{-3} mol/l was added portionwise to the suspension. A solution of 1% PVA was added, continuously stirring for 24 h. The silver catalysts were obtained after filtration, washing and drying at 80 °C, labeled as 1%Ag/P25, 3%Ag/P25 and 3%Ag/silica.

X ray diffraction (XRD) measurements were performed using a Bruker D8 Advance diffractometer with a Cu K α radiation operated at 40 kV. The morphology of the samples was investigated by a JEM-2100 transmission electron microscopy (TEM). Light absorbance was measured by a UVIKON/XL UV–vis diffuse reflectance spectrometer

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(UV–vis). The silver content was measured by an OPTIMA 7000 DV inductively coupled plasma optical emission spectroscopy (ICP-OES).

The photocatalytic activity of the catalyst was investigated in an annular quartz reactor. A 500 W high pressure mercury lamp, peaking at 365 nm, was positioned in the inner quartz tube with a cooling jacket. A reflux condenser was connected to the outlet of the reactor. Oxygen was introduced in the reactor through bubbling. The catalyst of 0.25 g was added in methanol of 250 ml in each run. The reaction was carried out at 40 °C. Samples were collected at intervals of every two hours. The liquid products were qualified by a GC-MS and quantified by a GC-FID. The formation rate of methyl formate was calculated by the following Eq. (1).

$$Fr = \frac{C \times V}{M \times m \times t} \quad (1)$$

where

Fr	formation rate, $\mu\text{mol.g}^{-1}.\text{h}^{-1}$
C	methyl formate concentration, $\mu\text{g.ml}^{-1}$
V	volume of reactant, ml
M	molecular weight of methyl formate, 60.05 g.mol^{-1}
m	weight of catalyst, g
t	reaction time, h

3. Results

Fig. 1a shows the XRD patterns of P25 and the catalysts of silver supported on P25. Fig. 1b shows the XRD patterns of silica and the 3%Ag/silica catalyst. The peaks in the patterns in Fig. 1a and b at about 38°, 44°, 64° and 77° were attributed to the diffractions of the crystal faces of (111), (200), (220) and (311), respectively, of metallic silver in cubic phase. The intensity of the peaks corresponding to the diffractions of cubic silver crystal faces strengthened with increasing the silver loading.

Fig. 2 shows the TEM images of the catalysts. The particle sizes of titania (Fig. 2a and b) were 20–50 nm. The size distribution of the silver nanoparticles on the 1%Ag/TiO₂ catalyst (Fig. 2a) was 3–16 nm, the majority of them with sizes of 5–10 nm, and that on the 3%Ag/TiO₂ catalyst (Fig. 2b) was 3–18 nm, the majority of them with sizes of 5–10 nm as well. The silica particle sizes were 10–20 nm (Fig. 2c and d). The sizes of silver nanoparticles on the 3%Ag/SiO₂ catalyst distributed from 3 to 15 nm, and the majority of them were with sizes of 4–7 nm, a little smaller than those on titania.

Fig. 3a shows the UV–vis absorption spectra of P25 and the catalysts of silver supported on P25, as well as the UV–vis spectra

of silver nanoparticles (see inset in Fig. 3a), which were obtained by tailoring the spectrum of P25 from the corresponding spectrum of the catalyst. The onset of the absorption of P25 was about 400 nm. A broad absorption band extended from 400 to 800 nm in the spectrum of the 1%Ag/P25 or 3%Ag/P25 catalyst, and the peak position of both of the two bands lay in about 470 nm. The broad peaks were assigned to the SPR of silver particles [17,19,20,22]. The position of the peak is determined by the silver particle size, which will redshift with the increase of the silver particle size [22]. So the broadness of the peak indicates a wide size distribution of the silver nanoparticles on the catalyst. These results were consistent with the TEM observation.

Fig. 3b shows the UV–vis absorption spectra of silica and the 3%Ag/SiO₂ catalyst, as well as the spectrum of silver nanoparticles (inset in Fig. 3b), obtained by tailoring the spectrum of silica from the spectrum of the 3%Ag/SiO₂ catalyst. The silica exhibited no absorption band. The absorption at shorter wavelength was resulted from intense scattering [20,22]. The absorption of silver nanoparticles (see insets in Fig. 3a and b) started as a sharp absorption minimum at 320 nm, which corresponded to a minimum in the imaginary part of the refractive index for bulk silver [27]. The absorption spectrum corresponding to the SPR of silver nanoparticles extended from 320 nm to 800 nm, peaking at 380 nm. The peak was asymmetric and broadening, which was the feature of silver nanoparticles on silica [20,22].

The methyl formate concentrations with times on P25 and on the silver catalysts supported on P25 are shown in Fig. 4a. The maximum formation rates of methyl formate are shown in Fig. 4b. P25 seem be active for the production of methyl formate. But the formation rate of methyl formate only by UV irradiation (see Fig. 5) exceeded that on P25 under the same UV irradiation, suggesting that P25 was negative to the formation of methyl formate in this condition. However, the activity of the silver catalyst supported on P25 increased remarkably. The maximum formation rate of methyl formate increased by 7 times on the 1%Ag/P25 catalyst and by 20 times on the 3%Ag/P25 catalyst in 6 h of the reaction, compared with that on P25.

Fig. 5a shows the methyl formate concentrations with times and Fig. 5b shows the formation rates of methyl formate only by UV irradiation, on silica and on the 3%Ag/silica catalyst. UV light was slightly active to the formation of methyl formate, and the formation rate attained to 4034 $\mu\text{mol g}^{-1} \text{h}^{-1}$ in 10 h, but that on silica was only 2474 $\mu\text{mol g}^{-1} \text{h}^{-1}$. It indicates that silica itself at least did not show positive effect for the production of methyl formate. The 3%Ag/silica catalyst, however, exhibited a high methyl formate formation rate, reaching 23,460 $\mu\text{mol g}^{-1} \text{h}^{-1}$ in 10 h and increasing by 9.5 times compared with that on silica.

P25 and silica as well as the silver catalysts supported on P25 or silica were less active under visible light, no or trace methyl formate being observed during the reaction. Methyl formate could not be detected at

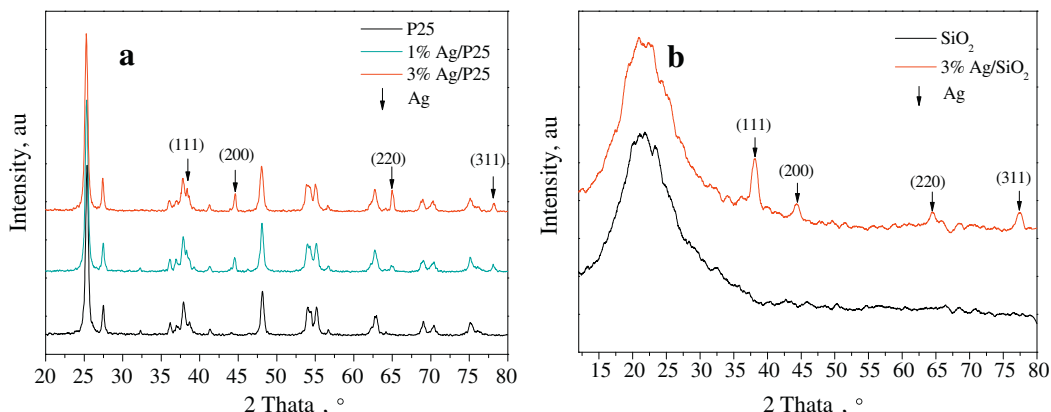


Fig. 1. XRD patterns of supports and catalysts. a-P25 and silver catalysts supported on P25; b-silica and silver catalysts supported on silica.

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