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Short Communication

Direct propylene epoxidation with H_2 and O_2 over In modified Au/TS-1 catalysts

Ji-Qing Lu *, Na Li, Xiao-Rong Pan, Chao Zhang, Meng-Fei Luo

Key Laboratory of the Ministry of Education for Advanced Catalysis Materials, Institute of Physical Chemistry, Zhejiang Normal University, Jinhua 321004, China

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ABSTRACT

A series of In promoted Au/TS-1 catalysts was prepared and tested for direct propylene epoxidation with H_2 and O_2. The In promotion could effectively enhance the reactivity and stability of the catalysts. A PO formation rate of 56 $g_{PO}\,h^{-1}\,kg_{cat}^{-1}$ was obtained over a 0.57Au/0.4In-TS-1 catalyst, which was about 80% enhancement compared to an un-promoted 0.25Au/TS-1 catalyst (32 $g_{PO}\,h^{-1}\,kg_{cat}^{-1}$). The enhancement was due to a higher Au capture efficiency by the modification of In on the TS-1 surface, and a higher dispersion of Au species in the catalyst.

1. Introduction

The direct propylene epoxidation to propylene oxide (PO) with H_2 and O_2 over gold catalysts supported on Ti-containing materials has been receiving much attention since it was first reported by the group of Haruta in 1998 [1]. This reaction is of great importance because it has the potential to replace the current commercial processes for PO production, such as the chlorohydrin process and organic hydroperoxide processes [2]. The Ti-containing supports applied for Au catalysts include titania [1] and various titanosilicates, such as Ti-MCM-41, Ti-TUD and Ti-HMS [3–5]. Recently, Au supported on microporous titanium silicalite-1 (TS-1) catalysts were found promising for this reaction as they were quite active and stable [6,7].

Although Au catalysts for direct propylene epoxidation have been extensively investigated in the past two decades, several key issues of this system must be concerned, such as low propylene conversion (usually <3%) and catalyst deactivation. One approach to the promotion of reactivity is modification of the catalyst by the addition of other elements in the catalysts. It was reported that treatment of the support with NH_4NO_3 [7], alkaline [8], alkaline earth metals [9] and silylation [10] could effectively promote the reactivity.

In this work, In promoted TS-1 supports were prepared and Au catalysts supported on these supports were tested for direct propylene epoxidation with H_2 and O_2. Enhanced reactivity was obtained on the In-promoted catalysts and was discussed based on the characterization results.

2. Experimental

2.1. Synthesis of TS-1, In-modified TS-1 and supported Au catalysts

The synthesis of TS-1 with a Ti/Si molar ratio of 1/100 was described in detail elsewhere [9]. The main chemicals used in the preparation were $Si(OC_2H_5)_4$ (TEOS, Sinopharm, AR), $Ti(OC_4H_9)_4$ (TBOT, Sinopharm, AR) and $(C_3H_7)_4N(OH)$ (TPAOH, Alfa Aesar, 20 wt.% aqueous solution). The In-modified TS-1 was synthesized by impregnating certain amount of $In(NO_3)_3$ solution (0.04 M, Sinopharm, 99.5 wt.%) with TS-1 for 3 h. The mixture was then dried by evaporation, followed by drying at 120 °C overnight and calcination at 500 °C for 3 h. Supported Au catalysts were prepared using the deposition–precipitation method. A 100 cm^3 solution of $HAuCl_4{\cdot}4H_2O$ (2 mg cm^{-3}, Jiuyue Chem., 99.8 wt.%) was heated to 70 °C under vigorous stirring. After adjusting the pH of the solution to 7 using a 0.1 M NaOH solution, 1 g of support (TS-1 or In-TS-1) was added, and the suspension was aged at 70 °C for 1 h. After cooling to RT, the solid was collected via centrifugation, washed with 10 cm^3 of deionized water, centrifuged again. The process was repeated for 5 times. Finally the solid was vacuum dried at RT overnight and the resulting solid was not further calcined. Actual Au, Ti and In contents in the catalysts were determined by inductively coupled plasma measurements, whereas the content of chlorine was measured by X-ray fluorescence spectrometry (XRF, ARLADVANT'X Intelli Power 4200). A catalyst designated as 0.57Au/0.4In-TS-1 indicates that the Au loading in the catalyst was 0.57 wt.% and In/Ti molar ratio of 0.4.

2.2. Characterizations

X-ray diffraction (XRD) measurements were carried out with a PANalytical X'Pert PRO powder diffractometer using CuKα radiation (40 kV, 40 mA). Transmission electron microscopy (TEM) images

* Corresponding author. Tel.: +86 579 82287325; fax: +86 579 82282595.
E-mail address: jiqinglu@zjnu.cn (J.-Q. Lu).

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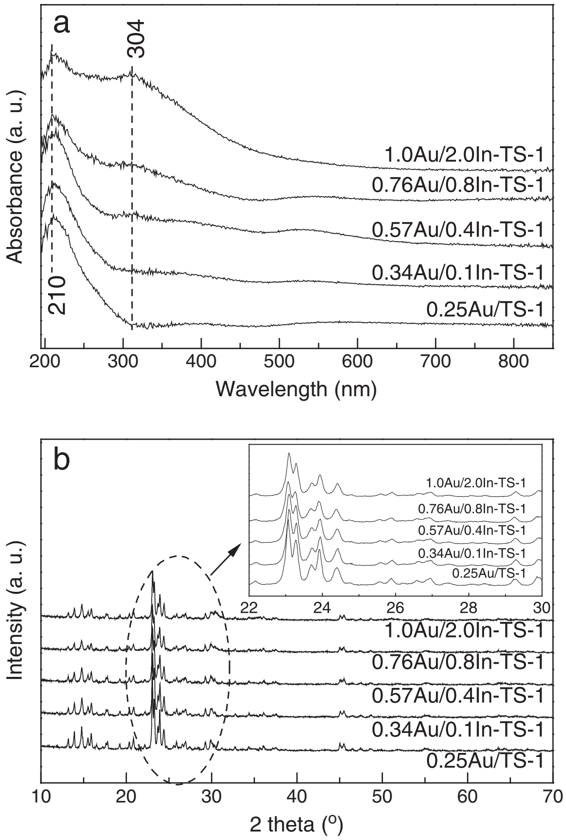

Fig. 1. a) UV–vis spectra and b) XRD patterns of Au/TS-1 with various In contents.

were obtained on a JEM2010 microscope (200 kV). The ultraviolet–visible spectra of the samples were collected on a Thermo Evolution 500 spectrophotometer. Fourier transform infrared (FTIR) measurements were carried out with a NEXUS 670 spectrometer provided with an MCT detector. Spectra were recorded at 4 cm^{-1} resolution and averaged 64 scans. X-ray photonelectron spectroscopy (XPS) experiments were carried out on a VG ESCALAB MK2 system with AlKα radiation. Binding energies were calibrated by using the contaminant carbon (C 1 s = 284.6 eV).

2.3. Catalytic testing

Epoxidation of propylene was carried out in a quartz tubular microreactor (i.d. = 8 mm, length = 180 mm) using 0.3 g catalyst of 100–140 mesh size without dilution. The catalyst was heated in a reaction gas mixture ($C_3H_6/H_2/O_2/N_2$ = 3.5/3.5/3.5/24.5 cm^3 min^{-1}) from RT to reaction temperature in 5 h. Products were analyzed online using a gas chromatograph (Shimazu GC-2014) equipped with a flame ionization detector and a thermal conductivity detector, attached respectively to a FFAP capillary column and a Porapak Q compact column. The following definitions were used.

Propylene conversion = moles of (oxygenates + CO_2/3)/moles of propylene in feed.

PO selectivity = moles of PO/moles of (oxygenates + CO_2/3).

3. Results and discussion

The prepared catalysts have surface areas of 380–400 m^2 g^{-1}, as determined by N_2 absorption at 77 K. XRF analyses indicate that Cl^- ions could be completely removed from the samples by washing during the preparation. UV–vis spectra of the samples (Fig. 1a) reveal that all the samples have strong absorption at 210 nm, implying the incorporation of Ti in the TS-1 matrix [11] and no crystalline TiO_2 is formed because of the absence of the absorption at ca. 330 nm. For the In-containing samples, one additional absorption peak at 304 nm is present and its intensity increases with In content in the sample, which could be assigned to the absorption of In_2O_3 [12].

Fig. 1b shows the XRD patterns of the catalysts. Diffraction peaks at 7.8, 8.8, 23.2, 23.8 and 45° are observed which are characteristic of TS-1. Furthermore, close examination (inset) confirms that there is no peak splitting at 24.4 and 29.4°, indicating the formation of well crystallized TS-1 with MFI structure [13]. In addition, no diffraction peaks due to Au species are detected, suggesting that the Au species are highly dispersed on the support.

Morphologies of the catalysts are characterized by TEM, as shown in Fig. 2. For the 0.25Au/TS-1 catalyst (Fig. 2a), the Au particle size ranges from 2 to 8 nm. For the 0.57Au/0.4In-TS-1 catalyst, the Au particle size is quite uniform (1–2 nm). While for the 1.0Au/2.0In-TS-1, more Au particles are detected and growth of Au particles occurs. It seems that appropriate amount of In addition helps the dispersion of Au particles (such as the 0.57Au/0.4In-TS-1), while large amount of In addition may result in the aggregation of Au particles.

Fig. 3 shows the Au 4f XPS spectra of the catalysts. The Au 4f core level spectra of the catalysts could be deconvoluted into several components at 83.6, 84.5 and 85.5 eV, which could be assigned to Au^0, Au^+ and Au^{3+} species, respectively [14]. Also, the contents of different Au species are estimated and shown in the figure. It is found that the In-promoted samples contain more oxidized Au species (Au^+ and Au^{3+}) than the 0.25Au/TS-1.

Table 1 lists the catalytic activities of the catalysts and the data were taken after 5 h reaction at 170 °C (quasi-steady state). The 0.25Au/TS-1 catalyst gives a propylene conversion of 2.0% and a PO selectivity of 87%, corresponding to a PO formation rate of 32 $g_{PO}h^{-1}kg_{cat}^{-1}$. After the addition of In, it can be seen that the propylene conversions increase, however, the PO selectivities are somehow suppressed. Among these catalysts, the 0.57Au/0.4In-TS-1 gives the highest propylene conversion (3.8%), corresponding to a PO formation rate of 56 $g_{PO}h^{-1}kg_{cat}^{-1}$. This indicates a 75% enhancement of PO production compared to the 0.25Au/TS-1. Further increasing In contents in the catalysts (such as the 1.0Au/2.0In-TS-1) result in a declined PO formation rate.

The catalysts were also investigated for stability. Fig. 4 shows the catalytic behaviors of the 0.25Au/TS-1 and the 0.57Au/0.4In-TS-1 catalysts. The 0.25Au/TS-1 catalyst gradually deactivates during the reaction, with an initial propylene conversion of 3.3% and 2.0% after about 7 h. For the 0.57Au/0.4In-TS-1 catalyst, it deactivates slightly

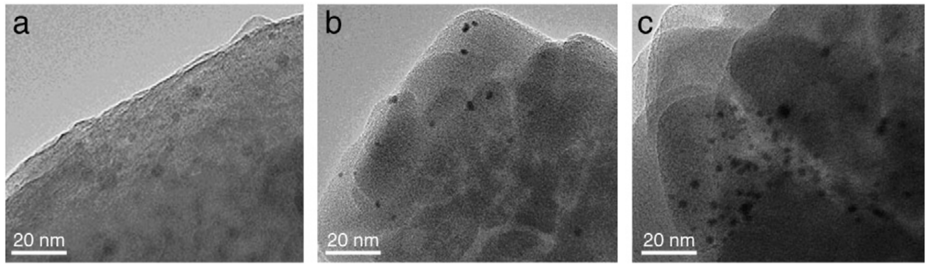

Fig. 2. TEM of images of (a) 0.25Au/TS-1, (b) 0.57Au/0.4In-TS-1, and (c)1.0Au/2.0In-TS-1.