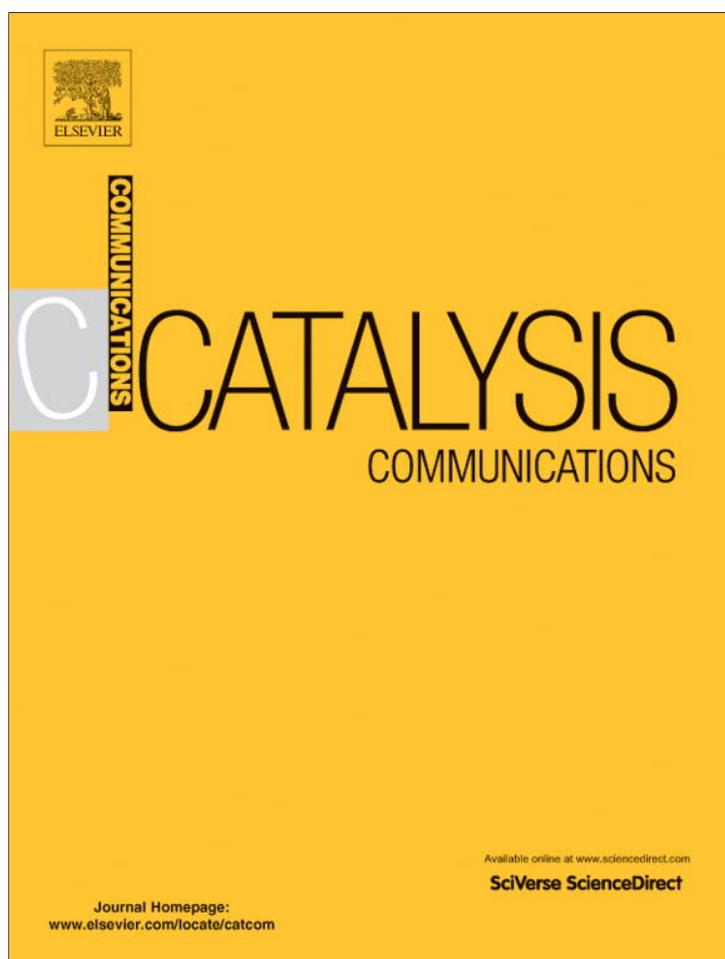


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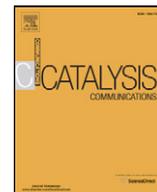
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Short Communication

Direct propylene epoxidation with H₂ and O₂ over In modified Au/TS-1 catalystsJi-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 H₂ and O₂. The In promotion could effectively enhance the reactivity and stability of the catalysts. A PO formation rate of 56 g_{PO}h⁻¹kg_{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⁻¹kg_{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.

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1. Introduction

The direct propylene epoxidation to propylene oxide (PO) with H₂ and O₂ 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 NH₄NO₃ [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 H₂ and O₂. 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(OC₂H₅)₄ (TEOS, Sinopharm, AR), Ti(OC₄H₉)₄ (TBOT, Sinopharm, AR) and (C₃H₇)₄N(OH) (TPAOH, Alfa Aesar, 20 wt.% aqueous solution). The In-modified TS-1 was synthesized by impregnating certain amount of In(NO₃)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 cm³ solution of HAuCl₄·4H₂O (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 cm³ 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, ARLADVANTX 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 CuK α 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).

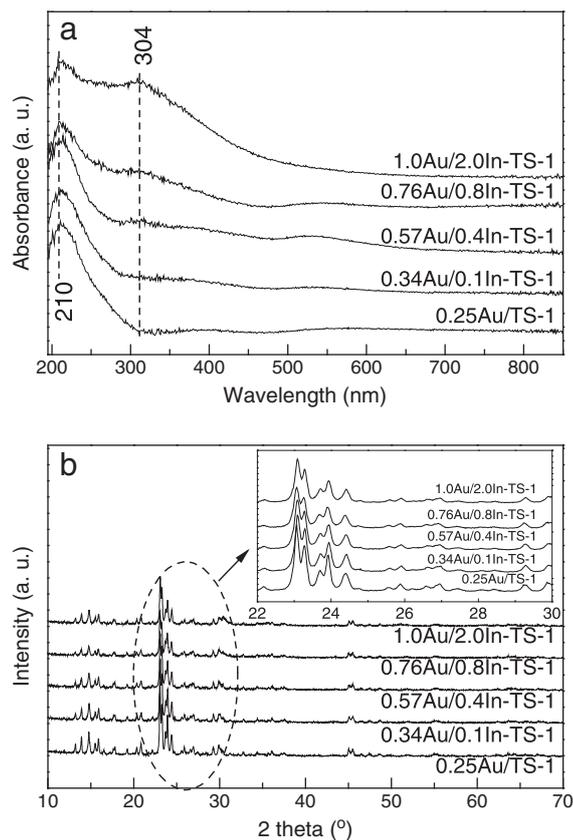


Fig. 1. a) UV-vis spectra and b) XRD patterns of Au/TS-1 with various In contents.

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 photoelectron spectroscopy (XPS) experiments were carried out on a VG ESCALAB MK2 system with AlK α 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 ($\text{C}_3\text{H}_6/\text{H}_2/\text{O}_2/\text{N}_2 = 3.5/3.5/3.5/24.5\text{ cm}^3\text{ min}^{-1}$) from RT to reaction temperature in 5 h. Products were analyzed on-line using a gas chromatograph (Shimadzu 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 + $\text{CO}_2/3$)/moles of propylene in feed.

PO selectivity = moles of PO/moles of (oxygenates + $\text{CO}_2/3$).

3. Results and discussion

The prepared catalysts have surface areas of $380\text{--}400\text{ m}^2\text{ g}^{-1}$, as determined by N_2 adsorption 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 $32\text{ g}_{\text{PO}}\text{ h}^{-1}\text{ kg}_{\text{cat}}^{-1}$. 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 $56\text{ g}_{\text{PO}}\text{ h}^{-1}\text{ kg}_{\text{cat}}^{-1}$. 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

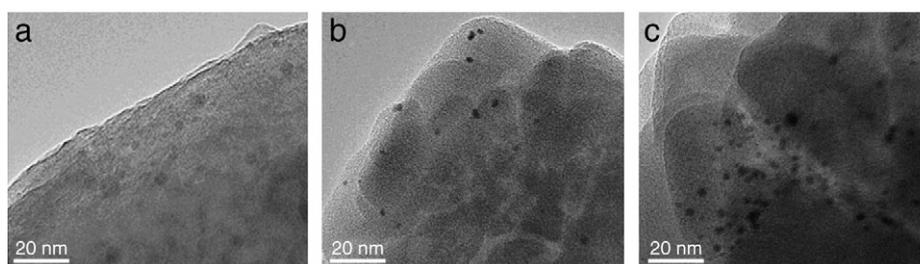


Fig. 2. TEM of images of (a) 0.25Au/TS-1, (b) 0.57Au/0.4In-TS-1, and (c) 1.0Au/2.0In-TS-1.

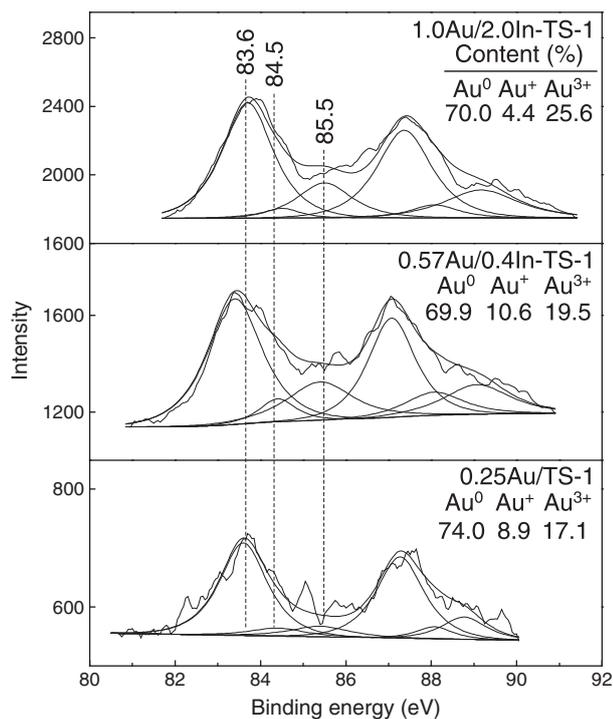


Fig. 3. Au4f XPS spectra of 0.25Au/TS-1, 0.57Au/0.4In-TS-1 and 1.0Au/2.0In-TS-1 catalysts.

during the reaction, with initial propylene conversions of 4.2% and 3.8% after about 7 h.

The deactivation of the Au catalysts for propylene epoxidation is commonly observed, mainly due to the oligomerization of the products on the catalyst surface [15]. Fig. 5 compares the FTIR spectra of the fresh and spent 0.25Au/TS-1 and 0.57Au/0.4In-TS-1 catalysts. For the 0.25Au/TS-1, significant band at 2980 cm^{-1} and a weak band at 2930 cm^{-1} appear after reaction, which are characteristic of C–H stretching vibrations of bidentate propoxy species [15]. While for the 0.57Au/0.4In-TS-1 catalyst, these two bands slightly increase in the intensities after reaction. This comparison implies that the deactivation of the 0.25Au/TS-1 is due to the strong adsorption of bidentate propoxy species on the catalyst surface via a ring open reaction of propylene oxide. On the contrary, the ring open reaction was much more suppressed on the 0.57Au/0.4In-TS-1 catalyst, deactivation is thus not so severe. Note that the adsorption of bidentate propoxy species on the catalyst is just one possibility that causes the catalyst deactivation, other possibilities such as the changes of oxidation states of Au species during the reaction could not be ruled out and need further investigation.

The catalytic results obtained on the In-promoted Au/TS-1 catalysts are comparable to those reported in literature. For example, Lu

Table 1
Effect of In-modification on epoxidation of propylene over Au/TS-1 catalysts.

Catalyst	Au content (wt.%)	X(C ₃ H ₆) %	S(PO) %	PO formation rate $\text{g}_{\text{PO}}\text{h}^{-1}\text{kg}_{\text{cat}}^{-1}$
0.25Au/TS-1	0.25	2.0	87	32
0.34Au/0.11In-TS-1	0.34	2.9	81	43
0.57Au/0.4In-TS-1	0.57	3.8	81	56
0.76Au/0.81In-TS-1	0.76	3.0	81	44
1.0Au/2.0In-TS-1	1.0	2.4	71	31

Reaction conditions: 170 °C, 0.1 MPa, C₃H₆:O₂:H₂:N₂ = 1:1:1:7 (35 $\text{cm}^3\text{min}^{-1}$), and GHSV = 7000 $\text{cm}^3\text{h}^{-1}\text{g}_{\text{cat}}^{-1}$

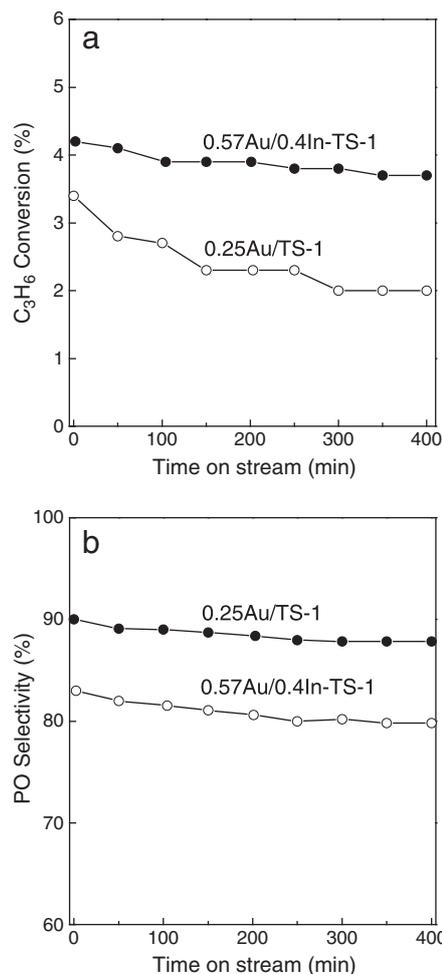


Fig. 4. Epoxidation of propylene on 0.25Au/TS-1(100) and 0.57Au/In-TS-1(100) catalysts.

et al. [9] reported a PO yield of 60 $\text{g}_{\text{PO}}\text{h}^{-1}\text{kg}_{\text{cat}}^{-1}$ on Ca-, Mg- and Sr-modified Au/TS-1 catalysts. And a PO yield of 29 $\text{g}_{\text{PO}}\text{h}^{-1}\text{kg}_{\text{cat}}^{-1}$ was reported on a Au-Ba/Ti-TUD catalyst [4]. The findings in the current work shows that the promotion of In in the Au/TS-1 catalyst could effectively enhance the reactivity, which could be interpreted by the higher Au capture efficiency in these samples compared to the bare Au/TS-1. Since the isoelectric point (IEP) of TS-1 is about 2–3 [16] and the pH value used in the catalyst preparation procedure

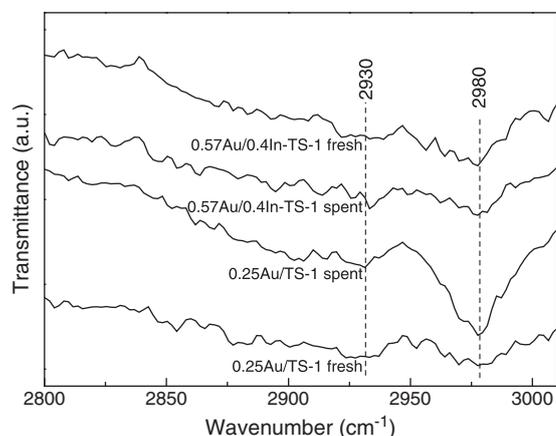


Fig. 5. FTIR spectra of fresh and spent 0.25Au/TS-1 and 0.57Au/0.4In-TS-1 catalysts.

is about 7, the negatively charged support surface would repulse the $[\text{Au}(\text{OH})_x\text{Cl}_{4-x}]^-$ ions, resulting in a low Au loading and Au capture efficiency. When the sample is promoted with In_2O_3 , the Au loading in the catalyst remarkably increases, due to the fact that the IEP of In_2O_3 is 9 and thus makes the support surface less negatively charged. Besides, it is also found that Au particles are smaller on the In-promoted catalyst compared to the unpromoted one, indicating that the addition of In_2O_3 helps the dispersion of Au particles in the catalyst by the interaction between Au and In cations, which could consequently increase the active sites. This might be another reason for the enhancement of reactivity on the In-promoted catalysts. However, too much In_2O_3 deposited on the TS-1 support (e.g. the 1.0Au/2.0In-TS-1) may cover the Ti sites and thus inhibit the reactivity. Besides, the In-promoted catalyst is more stable than the unpromoted one during the reaction, probably due to the coverage of some acidic Ti sites by In_2O_3 .

4. Conclusions

In this work, In-promoted Au/TS-1 catalysts were found to be active and stable for direct propylene epoxidation. The enhancement could be attributed to the higher Au capture efficiency and higher Au dispersion in the In-promoted catalysts compared to the bare Au/TS-1. This work demonstrates a new approach to prepare active Au/TS-1 catalysts using very dilute Au DP solutions, although In is more expensive than other metals such as Na, Mg and Ca as reported in Refs. [8,9].

Acknowledgments

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