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Au nanoparticles deposited on the external surfaces of TS-1: Enhanced stability and activity for direct propylene epoxidation with H_2 and O_2

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ABSTRACT

Au/TS-1 catalysts prepared by deposition–precipitation method are very promising for direct propylene epoxidation with H_2 and O_2. However, the catalysts usually suffer from rapid deactivation. In this work, calcined TS-1 with open micropores (TS-1-O) is first used to support Au catalysts, and then the used catalysts at different time-on-streams are characterized to understand the deactivation mechanism. The micropore blocking by carbonaceous deposits is found to be responsible for the deactivation. We therefore suggest a principle of catalyst design to improve the long term stability by depositing Au nanoparticles on the external surfaces of TS-1. For this purpose, uncalcined TS-1 with blocked micropores (TS-1-B) is used to support Au catalyst. As expected, the designed catalyst is not only very stable because of the elimination of pore blocking and the more accessible active sites, but also highly active with the PO formation rate of 125 $g_{PO}\ h^{-1}\ kg_{Cat}{}^{-1}$ for over 30 h.

1. Introduction

Propylene oxide (PO) as a versatile bulk chemical intermediate is widely used in the production of a variety of derivatives such as polyurethane and polyester resins. In view of the environmental and economic objectives, the direct epoxidation of propylene with molecular H_2 and O_2 for the synthesis of PO has attracted extensive interests compared to the chlorohydrin and peroxidation processes [1]. Encouraged by the finding of Au/TiO_2 catalyst with the high PO selectivity in despite of the low propylene conversion (ca. 1%) [2], great efforts have been devoted to developing active Au catalysts supported on Ti-containing materials [3–16]. Highly dispersed Au nanoparticles deposited on titanium silicate-1 (TS-1) with both the hydrophobic surfaces and the only presence of the isolated Ti (IV) sites were found to have much higher PO formation rate (116 ~ 160 $g_{PO}\ h^{-1}\ kg_{Cat}{}^{-1}$ at 200 °C) than those deposited on other Ti-containing supports [17,18]. As a result, the high formation rate of PO has been achieved to be comparable to that of ethylene oxide in commercial plants [19].

Despite the significant enhancement of the activity of Au/TS-1 catalysts, they usually suffer from rapid deactivation within several hours unless with very low Au loadings or carefully pretreated supports [18,20–22]. The aggregation of Au nanoparticles with time-on-stream proposed by Delgass and co-workers [9] was used to explain the deactivation. However, this interpretation was questioned by Lu et al. [23]. Instead, he explicated the deactivation by the blocking of active sites with the bidentate species and other organic fragments. However, no direct evidence was provided to relate the formation rate of the bidentate species to the deactivation rate over Au/TS-1 catalyst [17]. Thus, a better understanding of the deactivation mechanism is highly desired.

Recently, solid grinding (SG) [21,24] and sol-immobilization (SI) [22,25] methods have been used to prepare the Au/TS-1 catalysts. Although they show great stability, these catalysts have a low Au catalytic efficiency because some of the Au nanoparticles are deposited far away from the active titanium sites due to the non-selective deposition of Au nanoparticles [22,26]. Comparatively, the commonly used deposition–precipitation (DP) method is more attractive because Au nanoparticles can be selectively deposited near the active titanium sites by adjusting the pH of the solution higher than the isoelectric point of the inactive silicon sites [27,28]. When under similar Au particle size and without adding promoters, the PO formation rate of Au/TS-1 catalyst (160 $g_{PO}\ h^{-1}\ kg_{Cat}{}^{-1}$) prepared by DP method is much higher than those of Au/TS-1 catalysts prepared by SG and SI methods, which are 11 and 25 $g_{PO}\ h^{-1}\ kg_{Cat}{}^{-1}$, respectively [21,25]. It is expected that the Au/TS-1 catalysts prepared by DP method will show simultaneously enhanced activity and prolonged stability.

In this work, the deactivation mechanism of conventional Au/TS-1 catalysts (i.e., Au nanoparticles supported on calcined TS-1

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(TS-1-O) support) prepared by DP method is studied by characterization of used catalysts. The blocking of the micropores by carbonaceous deposits is found to be responsible for the catalyst deactivation. Analysis of the deactivation mechanism leads to a new strategy of the catalyst design to improve the catalyst stability by selectively deposition of Au nanoparticles on the external surfaces of TS-1. We therefore use uncalcined TS-1 with blocked micropores as the support in the hope that all the gold nanoparticles are on the exterior surface of the support. The so obtained catalyst (Au/TS-1-B) is evaluated and compared with Au/TS-1-O, which shows a significant improvement in the long term stability.

2. Experimental

2.1. Synthesis of Au/TS-1-B and Au/TS-1-O catalysts

TS-1 with the Si/Ti molar ratio of 100 was synthesized using the hydrothermal method developed by Khomane et al. [29]. The as-synthesized TS-1 was either directly used to support Au nanoparticles or calcined before supporting Au nanoparticles. The resulted two catalysts with blocked or open micropores were denoted as Au/TS-1-B and Au/TS-1-O, respectively.

In a typical process, 2.0 g polyoxyethylene 20-sorbitan monolaurate (Tween 20, Aldrich) was added to 28.6 mL deionized water under vigorous stirring, and then 22.6 g tetrapropylammonium hydroxide (TPAOH, 25 wt.%) and 173 mmol tetraethylorthosilicate (TEOS, 95 wt.%) were added into the above clear solution. Afterwards, 1.73 mmol titanium (IV) tetrabutoxide (TBOT, 99 wt.%) dissolved in 20 mL isopropanol (WAKO, 99.5 wt.%) was added dropwise. The solution was placed in Teflon autoclave at 443 K for at least 18 h. The as-synthesized TS-1 with template remaining in the micropores (i.e., TS-1-B) was washed and dried overnight at room temperature and calcined at 823 K for 5 h to yield TS-1-O which had open micropores.

The same DP procedures were used to support Au nanoparticles on TS-1-B and TS-1-O supports according to the previous report [17]. 10 mL $HAuCl_4 \cdot 3H_2O$ was dissolved in 40 mL deionized water, followed by the addition of 0.5 g TS-1-B or TS-1-O supports. The slurries of Au/TS-1-B and Au/TS-1-O were neutralized to pH of 7.3 by 1 M aqueous solution of sodium hydroxide and aged at room temperature for different times, i.e., 6.2 and 9.5 h, and the as-obtained Au/TS-1-B and Au/TS-1-O catalysts had Au loadings of 0.12 and 0.10 wt.%, respectively.

2.2. Catalyst characterization

The crystal phases of TS-1-B and TS-1-O supports were characterized by XRD (Rigaku D/Max2550VB/PC, Cu K_α radiation). The surface areas and pore volumes of the TS-1-B and TS-1-O supports were measured in a volumetric adsorption unit (Micromeritics ASAP 2020). The contents of carbonaceous deposits were obtained by thermogravimetric analysis (PerkinElmer TGA Pyris 1). The local environments of titanium in the TS-1-B and TS-1-O supports were determined by DRUV–vis (PerkinElmer Lambda 35) and FT-IR (Nicolet 6700). The zeta potentials of TS-1-B and TS-1-O supports were determined on a Delsa TM Nano C particle analyzer. The Au loadings of Au/TS-1-B and Au/TS-1-O catalysts were determined by AAS (ZEEnit 600). The transmission electron microscopy (TEM) images were obtained on a JEOL JSM-2100.

2.3. Catalytic testing

The Au/TS-1-B and Au/TS-1-O catalysts were tested for the gas-phase propylene epoxidation under atmospheric pressure in a quartz tubular reactor (i.d., 8 mm) using a feed containing C_3H_6, H_2, O_2 and N_2 with the flow rate of 3.5/3.5/3.5/24.5 mL min^{-1} (corresponding to a space velocity of 14,000 mL h^{-1} g$_{cat}{}^{-1}$), where 0.15 g catalysts of 60–80 mesh size were loaded. The two catalysts were heated from room temperature to 200 °C at a rate of 0.5 °C min^{-1}. The catalytic tests as a function of time-on-stream in this work started after the reaction temperature reached 200 °C. The reactants and products were analyzed by two on-line GCs (Agilent 6890), equipped with TCD (5A column and Porapak Q column) and FID (Porapak T column), respectively. The 5A (3 mm × 3 m) and Porapak Q columns (3 mm × 3 m) were used to detect hydrocarbons, H_2, O_2, N_2, CO_x and H_2O, while the Porapak T column (3 mm × 3 m) was used to detect oxygenates (e.g. propylene, propane, acetaldehyde, PO, acetone and propanal). Blank tests indicated that no PO was generated in the blank reactor.

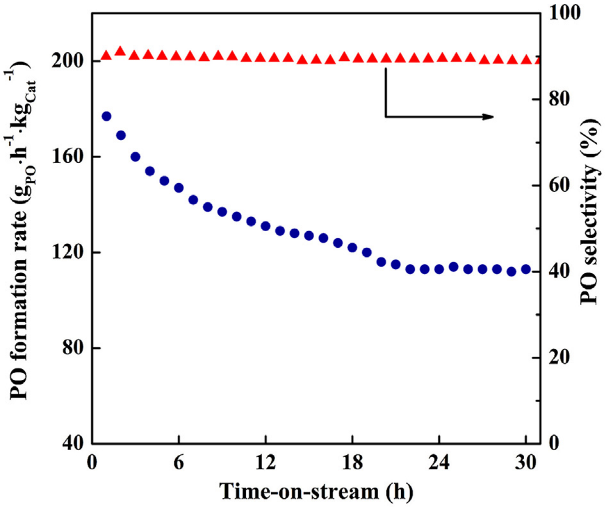

Fig. 1. PO formation rate and selectivity of 0.10 wt.% Au/TS-1-O catalyst as a function of time-on-stream.

3. Results and discussion

3.1. Deactivation behavior of Au/TS-1-O catalyst

Fig. 1 shows the PO formation rate of 0.10 wt.% Au/TS-1-O catalyst with time-on-stream. The selectivity to propylene oxide is nearly constant at 90%, while the PO formation rate decreases in different rates for the first 24 h, and then remains almost unchanged from 24 to 30 h. This unique deactivation phenomenon can be explained by different deactivation mechanisms, in which Au sintering and carbonaceous deposits formation on different catalysts sites are among the possible deactivation mechanisms [9,17,23]. Characterization of used catalysts at different time-on-streams (e.g., TEM, TGA, and N_2 physisorption) [9,17,23,30–34] is necessary to elucidate the deactivation mechanism of Au/TS-1-O catalyst during the propylene epoxidation reaction.

The average sizes of the gold nanoparticles on Au/TS-1-O catalysts used at 200 °C for 4 and 30 h are almost the same, as indicated by TEM images (Fig. S1). The negligible change in Au particle size was also observed by Lu et al. [23]. This excludes the aggregation of Au as the dominating deactivation mechanism. Fig. 2a shows the PO formation rate divided by the initial PO formation rate (R/R_0) as a function of the content of carbonaceous deposits. With the increase of carbonaceous deposits, the PO formation rate decreases in an exponential curve, implying that the deactivation of Au/TS-1-O catalyst is due to the formation of carbonaceous deposits. The deactivation modes of the 0.10 wt.% Au/TS-1-O catalyst by the carbonaceous deposits may be the active site coverage and/or the pore blocking, which can be discriminated