



Effect of Ti incorporated MWW supports on Au loading and catalytic performance for direct propylene epoxidation



Fang Jin^{a,b}, Yuanxin Wu^a, Shaowen Liu^a, Tsung-Han Lin^b, Jyh-Fu Lee^c, Soofin Cheng^{b,*}

^a Key Laboratory for Green Chemical Process of Ministry of Education, School of Chemical Engineering and Pharmacy, Wuhan Institute of Technology, Wuhan 430073, China

^b Department of Chemistry, National Taiwan University, Taipei 10617, Taiwan

^c Research Division, National Synchrotron Radiation Research Center, Hsinchu 300, Taiwan

ARTICLE INFO

Article history:

Received 5 May 2015

Received in revised form 13 August 2015

Accepted 20 August 2015

Available online 26 September 2015

Keywords:

MWW

Porosity

Ti coordination

Propylene epoxidation

ABSTRACT

Two types of novel catalysts consisting of gold nanoparticles (NPs) supported on the Ti-incorporated MWW structures were compared. One is Ti-YNU-1 with 0.67 nm micropores between expanded 2D-MWW structures, and the other is the titanosilicate pillared MCM-36 (Si/Ti-MCM-36) with 2 nm mesopores. The influences of pore structure and Ti coordination environment on the particle size of anchored Au NPs and their catalytic performances in propylene epoxidation with mixtures of H₂ and O₂ were investigated. The catalyst materials were characterized with Electron Probe Micro Analysis, X-ray diffraction, nitrogen sorption, UV–visible diffuse reflectance spectroscopy, transmission electron microscopy, and X-ray absorption spectroscopy. The coordination environment of Ti(IV) in Ti-YNU-1 is mainly isolated tetrahedral (T_d), while that in Si/Ti-MCM-36 was found to be a mixture of T_d and octahedral (O_h). The Au loading was proportional to the amount of Ti incorporated in the porous silica. The particle size of Au NPs in the Si/Ti-MCM-36 support was a little larger than that in the Ti-YNU-1 support, and it is attributed to that the highly isolated T_d Ti(IV) in Ti-YNU-1 is favorable for attaining the smaller gold NPs, while the higher loading of Ti in Si/Ti-MCM-36 anchored more Au and resulted in the formation of larger Au particles. On the other hand, the mesopores in Si/Ti-MCM-36 facilitated the diffusion of the produced PO in pore structure, inhibited the further reaction for side product formation, and moderated the deactivation of catalysts.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

The development of an efficient catalyst for the production of propylene epoxide (PO) is still an industrialization challenging work, since Haruta and coworkers [1] discovered for the first time that propylene epoxidation could be achieved with hydrogen and oxygen on-site generating H₂O₂ over gold nanoparticles supported on TiO₂ in 1998. PO is a very important feed stock in chemical industry and widely used to produce a variety of derivatives such as polyurethane, propylene glycol, polyester resins and surfactants. The direct epoxidation of propylene with co-reactants hydrogen and oxygen demonstrates an obvious advantage than the conventional ones, such as chlorohydrins, organic peroxide processes, and the direct epoxidation of propene with H₂O₂ over TS-1. The new process does not suffer from generating either

environmentally unfriendly chlorinated compounds, co-products with lower demand and/or market values or expensive cost of the oxidant H₂O₂ and its handling problems [2].

Therefore, the direct epoxidation of propylene to PO has gained considerable attention in the past seventeen years. For the direct propylene epoxidation over Au–Ti catalysts, it is generally agreed that the size of Au particles and the nature of the titanium-containing supports are important factors to the activity of the catalysts. Various titanosilicates, including TiO₂/SiO₂ [3], Ti-TUD [4], Ti-SBA-15 [5], Ti-MCM-41 [6], Ti-MCM-48 [7], Ti-MWW [8], Ti-β [9], TS-2, TS-1 [10,11], and alkaline treated TS-1 [12] have been investigated for propylene epoxidation. Chowdhury et al. [13] declared that Au particles supported on anatase TiO₂ of 2–5 nm in size were responsible for epoxidation, whereas particles smaller than 2 nm were responsible for hydrogenation to form propane and those larger than 5 nm were responsible for propylene combustion. Later, Haruta's groups proposed that the dominant gold active sites in Au/TS-1 for the PO reaction might be 55 gold atom clusters of ca. 1.4 nm diameter [14]. Recently, Feng et al.

* Corresponding author.

E-mail address: chem1031@ntu.edu.tw (S. Cheng).

[15] identified the size-dependent activity of Au nanoparticles (2–5 nm) deposited on the exterior surface of TS-1 by employing uncalcined TS-1. The catalyst with Au nanoparticles about 2.5 nm was reported to have the best catalyst performance. Although many studies have addressed the issue, the assignment of the gold active sites is still under debate. Moreover, the effect of pore size of support on the epoxidation is much interesting for the researcher.

The MCM-22 zeolite (IZA code MWW) is first identified by Leonowicz et al. [16] in 1994 to have the crystalline structure formed by vertically aligning lamellar zeolite intermediate, and the material was patented in 1990 by Rubin and Chu [17] in Mobil. The zeolitic MWW structure comprises two independent 10-membered ring (MR) channels and 12-MR cups on the crystal exterior, which lamellar structure exhibits advantages of high flexibility in varying the pore structures by different post-treatments [18]. In 1988, Bellussi et al. [19] reported the synthesis of a borosilicate zeolite (ERB-1), which is actually isostructural with the MCM-22 aluminosilicate [20]. Furthermore, Wu et al. [21] and Fan et al. [22] synthesized the titanosilicate zeolites, Ti-MWW and Ti-YNU-1, respectively, using ERB-1 as the precursor. Ti-YNU-1 has the same basic building unit as Ti-MWW with 3D MWW micropore structures but an expanded interlayer window from 10 to 12-MR and an enlarged 2.59 Å interlayer spacing [23,24]. Ti-incorporated MWW structures have attracted scientists because of their catalytic properties in partial oxidation reactions [18]. Recently, a new approach for preparing Ti incorporated MCM-36 material (Si/Ti-MCM-36) was developed in our laboratory by intercalating the ERB-1 with titanosilicate pillars [25].

The generated Si/Ti-MCM-36 has pillared 2 nm mesopores and higher surface area than Ti-YNU-1. This new development provides a very good chance to find the effect of pore structure on the supported Au catalysts on direct propylene epoxidation by comparing the performances of Au/Si/Ti-MCM-36 and Au/Ti-YNU-1, which are both of MWW structure.

2. Experimental methods

2.1. Preparation of materials

The hydrothermal synthesis of borosilicate MWW structure, i.e., ERB-1 precursor (ERB-1(P)) was initially prepared following the synthesis method reported by Millini et al. [26] with the ratio of Si:B:piperidine (PI):H₂O = 1:0.75:1.4:19.

Titanosilicate Ti-YNU-1 and Ti-MWW were prepared by re-hydrothermal synthesis method described in the literature [22,23,27]. This process includes sequential steps for the synthesis of ERB-1 precursor, deboronation with 2 M HNO₃ aqueous solution, and post-hydrothermal treatment at 443 K under a rotating condition for 5 days, with highly deboronated ERB-1 zeolite, tetrabutylorthotitanate (TBOT), piperidine (PI) and water in molar composition of Si:Ti:PI:H₂O = 1.0:0.01:1:15. The as-synthesized precursors were then refluxed in 2 M HNO₃ solution at 373 K for 6 h with solid to liquid ratio of 1/50 and further calcined at 823 K for 10 h to obtain a lamellar titanosilicate with a structure analogous to the MWW precursor and denoted as x-Ti-YNU-1, where x is the Si/Ti molar ratio in the pillaring gel. Furthermore, another 6 h acid treatment of 100-Ti-YNU-1 with 2 M HNO₃ solution at 373 K resulted in the sample A-Ti-YNU-1. An attempt for synthesis of high Ti contents Ti-YNU-1 was also carried out with similar procedure as that 100-Ti-YNU-1, with the post-hydrothermal molar ratio of Si:Ti:PI:H₂O = 1.0:0.03:1:15. The generated sample is denoted as 33-Ti-YNU-1.

The synthesis of Si/Ti-MCM-36 started with a swelling step with ERB-1 in the presence of tetrapropylammonium hydroxide (TPAOH) and cetyltrimethylammonium bromide (CTMABr) with a

relative weight ratio of TPAOH:CTMABr:H₂O = 1:4:330. The mixture was sealed in a flask at 373 K for 16 h. The swollen ERB-1 material recovered by filtration, washing with distilled water, and drying under vacuum was dispersed in a mixture of tetraethylorthosilicate (TEOS) and TBOT with TEOS/TBOT molar ratio of 100:1, and 160:1, then the mixture was stirred at 353 K for 25 h. The material was then filtered and dried at ambient condition. The hydrolyzation of TBOT and TEOS was carried out by suspending the dried solid in an aqueous solution at 313 K for 6 h at pH 9 adjusted by 1 M NH₃·H₂O. Finally, the sample was calcinated at 723 K for 3 h in nitrogen and at 812 K for 6 h in air (heating rate of 2 K min⁻¹). The resultant materials were designated as xSi/Ti-MCM-36, where x is the Ti/Si molar ratio in the pillaring gel.

Gold was deposited on the supports by a deposition-precipitation (DP) method using sodium hydroxide. Approximately, 0.1 g of HAuCl₄·3H₂O (Alfa Aesar, 99.99%) was dissolved in 25 mL of D.I. water stirring at 313 K, and a 0.1 M NaOH was added to target the final pH of the gold solution to pH 6. The gold solution was nearly colorless, indicating that most of the chloride ligands were replaced by the hydroxyl ligands [28,29]. The neutralized gold solution was further stirred for 2 h at 313 K. After this, 0.35 g of the support was added, and the suspension was stirred. Then 0.1 M NaOH was added to control the pH 7 for about 1 h, and the mixture was stirred for another 2 h at the same temperature and pH value. The solid was filtered and washed with 500 mL of D.I. H₂O, dried under ambient for 12 h. The prepared catalyst precursors were stored in sealed amber bottles at 277 K. Before catalytic performance they were packed into the reactor to reaction. The sample was designated mAu/x-Ti-YNU-1 or mAu/xSi/Ti-MCM-36, where m represents a nominal content of m wt% of gold on this catalyst. The m = 1.5 and 4.5 is corresponding to the Au³⁺ precursor concentration in the DP solution around 1.1 × 10⁻³ M and 3.3 × 10⁻³ M.

2.2. Characterization

X-ray powder diffraction patterns were recorded using a PANalytical X'Pert PRO diffractometer with a Cu-K_α radiation (λ = 1.5418 Å) operated at 40 mA and 45 kV. N₂ sorption isotherms were measured at 77 K on a Micromeritics TriStar 3000 analyzer after vacuum pretreating the samples at 473 K for 8 h. Total specific surface areas (S_{BET}) were calculated using the Brunauer–Emmett–Teller (BET) method, and the total pore volume (V_{total}) was evaluated from N₂ uptake at a relative N₂ pressure of 0.99. The t-plot was employed to evaluate the volume of micropores (V_{micro}). The corresponding pore size distribution (PSD) was determined using the desorption branches of the isotherms by Barrett–Joyner–Halenda (BJH) method. Diffuse reflectance (DR) UV–vis spectra were recorded using a Hitachi U-3310 spectrometer equipped with an integrating sphere detector, and BaSO₄ was the reference. The elemental analyses were determined using Electron Probe Micro Analysis (EPMA) in JEOL JXA-8200 Electron Probe. The EPMA results are determined by Wavelength Dispersive Spectrometer (WDS), which can give an accurate quantitative analysis of element. Transmission electron microscopy (TEM) photographs were obtained from a JEOL JEM-1200EX II Transmission Electron Microscope and Hitachi H-7100 Transmission Electron Microscope.

Au_{LIII}-edge X-ray absorption spectra (XAS) were collected using the fluorescence mode at the beam lines 17C of the National Synchrotron Radiation Research Center (NSRRC) facility in Hsinchu, Taiwan. Standard operating condition was 1.5 GeV and 350 mA. The photon energy was guided using a fixed-exit double-crystal Si(111) monochromator and calibrated with a metallic Au foil (L_{III}-edge, 11,919 eV).

Download English Version:

<https://daneshyari.com/en/article/53302>

Download Persian Version:

<https://daneshyari.com/article/53302>

[Daneshyari.com](https://daneshyari.com)