# Au/uncalcined TS-1 Catalysts for Direct Propene Epoxidation with H<sub>2</sub> and O<sub>2</sub>: Effects of Si/Ti Molar Ratio and Au Loading

Xiang Feng<sup>a</sup>, Xuezhi Duan<sup>a</sup>, Jia Yang<sup>a</sup>, Gang Qian<sup>a</sup>, Xinggui Zhou<sup>a,\*</sup>, De Chen<sup>b</sup>,

Weikang Yuan<sup>a</sup>

<sup>a</sup> State Key Laboratory of Chemical Engineering, East China University of Science and Technology, 130 Meilong Road, Shanghai 200237, China

<sup>b</sup> Department of Chemical Engineering, Norwegian University of Science and Technology, Trondheim 7491, Norway

**Abstract:** For direct propene epoxidation with  $H_2/O_2$ , TS-1 with blocked micropores (TS-1-B) is recognized as an attractive support for Au catalysts with enhanced stability and activity by suppressing the deactivation caused by micropore blocking. In this work, as a consecutive effort, effect of Si/Ti molar ratio of TS-1-B on catalytic performance is investigated. It is shown that the optimum Si/Ti molar ratio is 40. In other words, both lower and higher ratios are unfavorable for the formation of propylene oxide, which are possibly attributed to the presence of extra-framework Ti species and the difficult transmission of hydroperoxide species from Au surface to nearby Ti sites, respectively. Based on this, effect of Au loading on catalytic performance is further examined. When the Au loading is 0.13 wt%, the catalyst shows not only high PO formation rate of 158 gPoh<sup>-1</sup>kg<sub>Cat</sub><sup>-1</sup> comparable to the reported best activity without adding promoters, but also significantly enhanced stability at 200 °C over 30 h.

**Keywords:** Propene epoxidation; Uncalcined TS-1; Si/Ti molar ratio; Au loading; Stability

<sup>\*</sup>Corresponding author. Tel.: +86-21-64253509. Fax.: +86-21-64253528. E-mail address: xgzhou@ecust.edu.cn

# **1** Introduction

Direct propene epoxidation with molecular  $H_2$  and  $O_2$  to synthesize propylene oxide (PO) is a greener, simpler and more sustainable route compared with traditional chlorohydrin and several organic hydroperoxide processes [1-4]. In 1998, Haruta and coworkers first reported that Au/TiO<sub>2</sub> catalyst could achieve high PO selectivity for this reaction at low temperature. However, the catalyst showed low conversion [1, 5]. Subsequently, highly dispersed Ti species of the support in the form of isolated tetrahedral coordination was found to make the catalyst more active [6], and these isolated Ti<sup>4+</sup> sites could interact with hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) formed on Au nanoparticles to generate Ti-OOH species, which further selectively oxidize propene to PO [7, 8]. Since then, considerable efforts have been devoted to developing isolated Ti<sup>4+</sup>-containing materials (e.g., TS-1, Ti-SiO<sub>2</sub>, Ti-HMS and Ti-3D mesoporous titanosilicates) to support Au nanoparticles in the hope of improving the catalytic performance [9-25].

For the isolated Ti<sup>4+</sup>-containing materials supported Au catalyst, the catalytic performance is significantly affected by Si/Ti molar ratio [18, 20, 26-28]. For example, Yuan et al. reported that Si/Ti molar ratio of 20 favored the formation of PO for Au/Ti-hexagonal mesoporous molecular sieves catalyst [29]. Delgass et al. found Si/Ti molar ratio of 100 was the optimum value for TS-1 with open micropores [26]. It should be noted that the reported mesoporous Ti-containing supports usually have low hydrophobicity which results in the adsorption and oligomerization of PO on the surface of support, and thus leads to severe deactivation [17, 21]. In addition, for the micropores. Under reaction condition, the micropores of the support will be blocked

by carbonaceous coke and make Au clusters inside the channels inaccessible to reactants, which eventually results in deactivation [9]. Moreover, some highly active and tiny Au clusters in the micropores cannot be viewed by HRTEM [30, 31]. Hence, for the catalysts with the same Au loading but different Si/Ti molar ratio, the trend for the change in the percentage of Au clusters in the micropores is unclear. All of the above results will hinder the identification of intrinsic effect of Si/Ti molar ratio on catalytic performance. Therefore, using a highly stable and nonporous catalyst to probe the intrinsic effect of Si/Ti molar ratio on the catalytic performance is highly desirable.

Along this line, uncalcined TS-1 with blocked micropores (TS-1-B) supported Au catalyst [9, 10, 32, 33] provides the possibility to fulfill this target. On the one hand, it is highly stable because the support is hydrophobic and Au nanoparticles are deposited on the external surfaces of the support, avoiding the deactivation caused by PO adsorption and micropore blocking. On the other hand, its nonporous characteristic could guarantee all Au clusters have uniform size and viewed on the external surfaces of the support. Therefore, it is feasible to accurately correlate the catalytic performance with Si/Ti molar ratio by using Au/TS-1-B catalyst.

Herein, TS-1-B supports with different Si/Ti molar ratios ranging from 20 to 200 are synthesized, and then used to support Au nano-catalysts for direct propene epoxidation with H<sub>2</sub> and O<sub>2</sub>, in which the Au loadings and observable Au average particle size are similar. Effects of Si/Ti molar ratio on activity and selectivity are investigated, and possible structure-performance relationship is correlated. Using TS-1-B with the optimized Si/Ti molar ratio, Au/TS-1-B catalysts with different Au loadings are prepared and used for the reaction. The optimized Au/TS-1-B catalyst shows significantly enhanced activity of 158  $g_{PO}h^{-1}kg_{Cat}^{-1}$  and high stability over 30 h. The

insights reported here may be of great significance to the design and development of highly active and stable Au/Ti-containing catalyst.

## **2** Experimental

#### 2.1 Synthesis of Au/TS-1-B catalysts

TS-1 supports with blocked micropores (TS-1-B) were synthesized according to the previously reported method [9]. Different Si/Ti molar ratios were tuned by changing the amount of titanium (IV) tetrabutoxide (TBOT, 99 wt%). The synthesized TS-1-B support with Si/Ti molar ratio of x is labeled as TS-1-B(x).

Au/TS-1-B catalysts were prepared by deposition-precipitation method [9, 26]. 0.1 g hydrogen tetrachloroaurate(III) trihydrate (HAuCl<sub>4</sub>·3H<sub>2</sub>O, Sinopharm Chemical Reagent Co., Ltd, 99.99%) was dissolved in 40 mL deionized water, followed by addition of 0.5 g TS-1-B. The Au/TS-1-B slurry was neutralized to pH of 7.0-7.5 by 1 M aqueous solution of NaOH (Sinopharm Chemical Reagent Co., Ltd, 96%) and aged at room temperature for required hours to tune the Au loadings. The solid catalysts were collected by centrifugation (4000 rpm for 30 min) and washed twice with deionized water, and then dried under vacuum at room temperature for 12 h.

#### 2.2 Characterization

X-ray diffraction (XRD) was performed on a Rigaku D/Max 2550VB/PC diffractometer using Cu K $\alpha$  radiation. Ultraviolet-visible spectroscopy (UV-vis) was carried out on a Perkin-Elmer Lambda 35 spectrometer equipped with a diffuse-reflectance accessory, using BaSO<sub>4</sub> as a reference. Fourier transform infrared spectroscopy (FT-IR) was performed on a Nicolet 6700, where the TS-1-B samples

were ground with KBr. HRTEM characterization was carried out for reduced catalysts on a JEOL JEM 2100F with accelerating voltage of 200 kV. Metal particle sizes and distributions were determined by measuring more than 150 randomly selected particles. N<sub>2</sub> physisorption was measured in a Micromeritics ASAP 2020. Atomic absorption spectroscopy (AAS) was carried out using a ZEEnit 600 spectroscopy for elemental analysis.

#### 2.3 Catalytic testing

Gas-phase propene epoxidation was carried out under atmospheric pressure in a quartz tubular reactor (i.d., 8 mm) loaded with 0.15 g catalysts of 60-80 mesh size. The gas feed passing through the reactor has a concentration of 10/10/10/70 vol.% for C<sub>3</sub>H<sub>6</sub>, H<sub>2</sub>, O<sub>2</sub> and N<sub>2</sub>, respectively and a space velocity of 14,000 mLh<sup>-1</sup>g<sub>cat</sub><sup>-1</sup>. The Au/TS-1-B catalysts were slowly heated from room temperature to 473 K at a rate of 0.5 K min<sup>-1</sup> and then kept at 473 K for reaction. The concentrations of reactants and products were measured online by two on-line Agilent 6890 GCs equipped with TCD (Porapak Q and 5A columns) and FID (Porapak T column) detectors.

## **3 Results and discussion**

#### 3.1 Effect of Si/Ti molar ratio on the catalytic performance of Au/TS-1-B catalysts

Textural properties of TS-1-B supports with different Si/Ti molar ratios (i.e., 20, 40, 50, 90, 100, 150 and 200) are characterized by  $N_2$  physisorption, and the results are shown in Table 1. TS-1-B supports with Si/Ti molar ratios ranging from 20 to 200 show low BET surface areas and negligible micropore volumes, indicating the nonporous characteristics of the supports. This is because the micropores are blocked by TPA

templates (i.e., TPA<sup>+</sup>) which reside in the channel intersection with the propyl groups extending along the channels [34].

(Table 1 should be inserted here)

Fig. 1 shows XRD patterns of TS-1-B supports with different Si/Ti molar ratios. All the supports show the disappearance of splitting peaks at 24.5°, indicating that they exhibit the well-developed MFI structure with orthorhombic symmetry [4, 35]. Fig. 2 shows FT-IR spectra of different TS-1-B supports. The characteristic bands of framework Ti species at 960 cm<sup>-1</sup> are assigned to the stretching vibration of Si-O-Ti bonds [36, 37], which confirms that titanium is incorporated into the MFI framework. The coordination state of the incorporated Ti species was investigated by UV-vis spectroscopy and the results are shown in Fig. 3. The adsorption peaks of framework Ti (IV) at 220 nm are ascribed to the isolated Ti<sup>4+</sup> species in the TS-1 structure. Other adsorption peaks at 250 and 330 nm are related to the presence of Ti species in penta- or hexahedral coordination and extra framework anatase phases, respectively [37-39]. For the TS-1-B supports with Si/Ti molar ratio ranging from 40 to 200, only adsorption peaks at 220 nm are observed, indicating that the titanium species in the framework are all isolated Ti<sup>4+</sup> species [9]. The slightly reduced intensity of band at 220 nm with the increase of Si/Ti molar ratio is mainly due to the reduced Ti<sup>4+</sup> contents in the framework. However, further decreasing the Si/Ti molar ratio to 20 results in the presence of unfavorable Ti species in anatase phase.

(Fig. 1 should be inserted here)

(Fig. 2 should be inserted here)

#### (Fig. 3 should be inserted here)

The TS-1-B supports with different Si/Ti molar ratios are used to prepare Au catalysts by the widely used deposition-precipitation method. All the catalysts have the same Au loadings of 0.10 wt% by adjusting Au slurry aging time. In addition, the Au catalysts after reaction are characterized by HRTEM and the average Au particle sizes are similar (Fig. S1). As a result, the Au size effect on catalytic performance can be excluded. The synthesized Au/TS-1-B catalysts are tested for propene epoxidation with H<sub>2</sub> and O<sub>2</sub>. Fig. 4a shows the PO formation rate and selectivity of Au/TS-1-B catalysts with different Si/Ti molar ratios. With the increase of Si/Ti molar ratio from 20 to 200, there is an increase in PO formation rate from 65 to 127 g<sub>PO</sub>h<sup>-1</sup>kg<sub>Cat</sub><sup>-1</sup>, followed by a gradual decrease to 51 g<sub>PO</sub>h<sup>-1</sup>kg<sub>Cat</sub><sup>-1</sup>. For Au/TS-1-B catalyst with Si/Ti molar ratio of 20, the titanium content exceeds the maximum value that TS-1 framework could accommodate (i.e., Si/Ti molar ratio of 39) [18, 40]. Hence a large number of non-desired extra-framework titanium species exist (Fig. 3), which facilitates the non-selective oxidation of propene to other oxygenate products [26, 27] and thus leads to low PO selectivity and PO formation rate. When all of the Ti species are isolated framework Ti<sup>4+</sup>, lower Si/Ti molar ratio is found to favor the formation of PO and the optimum Si/Ti molar ratio is 40 (Fig. 4a). This can be explained from the reaction mechanism. It is accepted that the synthesized  $H_2O_2$  (active oxygen species also for other reactions [41, 42]) by hydrogen and oxygen on Au sites could transfer to the nearby titanium sites to generate Ti-OOH intermediate for selective propene epoxidation, directly decompose to water or non-selectively oxidize propene to side products [7, 43]. When the titanium content is high (e.g., low Si/Ti molar ratio of 40), more as-synthesized H<sub>2</sub>O<sub>2</sub> could reach the nearby titanium centers rather than decompose to H<sub>2</sub>O. This results in more Ti-OOH intermediates used for propene

epoxidation and thus higher PO formation rate. In contrast, when the titanium content is low (e.g., high Si/Ti molar ratio of 200), a part of the H<sub>2</sub>O<sub>2</sub> species may not reach nearby Ti species and thus directly decompose to water or non-selectively oxidize propene to side products (Fig. 5). This can be further demonstrated by the lower H<sub>2</sub> selectivity of the Au/TS-1-B catalyst with higher Si/Ti molar ratio (Fig. 4b). When the Si/Ti molar ratio increases from 40 to 200, the H<sub>2</sub> selectivity decreases from 32 to 11%, indicating that the decomposition of H<sub>2</sub>O<sub>2</sub> and non-selective oxidation is facilitated on Au/TS-1-B with higher Si/Ti molar ratio. In addition, lower Si/Ti molar ratio could make the support more hydrophobic [26] and favor PO desorption. This may be another reason for the higher PO formataion rate of Au/TS-1-B catalysts with lower Si/Ti molar ratio.

#### (Fig. 4 should be inserted here)

#### (Fig. 5 should be inserted here)

It should be noted that the optimum Si/Ti molar ratio of TS-1-B (i.e., 40) concluded in this work is not in accordance with the reported optimum Si/Ti molar ratio (i.e., 100) of traditional TS-1 with open micropores [8, 11, 26]. For the two supports, the dominant difference is the pore structure. When traditional TS-1 with different Si/Ti molar ratios are employed as supports, highly active and tiny Au clusters could enter into the microporous channels. The ratio of Au clusters in the micropores and that on the external surfaces may vary with Si/Ti molar ratio and thus possibly results in an optimum Si/Ti molar ratio different from that for Au/TS-1-B catalysts.

#### 3.2 Influence of Au loading on activity and selectivity of Au/TS-1-B catalysts

In general, the PO formation rate is greatly affected by Au loading [18, 26, 44]. As

shown in Fig. 6, the PO formation rate first rises from 63 to 158  $g_{PO}h^{-1}kg_{Cat}^{-1}$  and then decreases to 135  $g_{PO}h^{-1}kg_{Cat}^{-1}$ . The initial increase of PO formation rate is primarily due to the increased number of Au active sites for H<sub>2</sub>O<sub>2</sub> formation. However, further increasing the Au loading generally results in larger Au particle size [10]. The larger Au nanoparticles have much lower percentage of Au active sites and hence show lower PO selectivity and PO formation rate per mole of Au [10]. As a result, when Au loading is higher than 0.13 wt%, the PO formation rate gradually decreases. Therefore, the interplay between amount of Au and Au particle size may contribute to the variation of PO formation rate. Without adding promoters, the 0.13 wt% Au/TS-1-B(40) catalyst could show high PO formation rate of 158  $g_{PO}h^{-1}kg_{Cat}^{-1}$ . To further increase the activity, strategy for synthesizing smaller-sized Au catalysts [45] could be explored. In addition, the PO selectivity keeps decreasing with the increase of Au loading from 0.05 to 0.50 wt%, which is also due to the larger Au particle size with the increase of Au loading [23].

#### (Fig. 6 should be inserted here)

The stability of Au/Ti-containing catalyst is always one of the dominant problems that hinder the commercialization of the direct propene epoxidation process [9]. The first reported Au/TiO<sub>2</sub> catalyst suffered from severe deactivation in only 3 h even at low reaction temperature (e.g., 100 °C) [1, 5, 46]. Au catalysts with much higher activities, such as Au/Ti-MCM-41, Au/Ti-MCM-48 and Au/Ti-SiO<sub>2</sub> [20-22] were reported after but still suffered from rapid deactivation because of the strong PO adsorption on the support, which facilitates oligomerization, rearrangement, cracking and coupling reactions [21]. Increasing the hydrophobicity of TS-1 enhanced the stability of Au catalyst [9, 14], but in the initial 20 h, the catalyst lost ca. 35% of the activity [9, 26].

The main cause for rapid deactivation may not be Au aggregation [27] but the micropore blocking by carbonaceous coke [9], which makes part of Au clusters inside microporous channels not accessible to reactants.

When TS-1-B with nonporous characteristic is used as support, Au nanoparticles are deposited on the external surfaces of TS-1 support. Hence the Au/TS-1-B catalyst exhibits good stability [9, 10]. As shown in Fig. 7, Au/TS-1-B catalysts with different Au loadings of 0.08, 0.10 and 0.13 wt% show similar high stability. To the best of our knowledge, the 0.13 wt% Au/TS-1-B(40) catalyst prepared by deposition-precipitation method shows the highest PO formation rate (158  $g_{PO}h^{-1}kg_{Cat}^{-1}$ ) and stability (over 30 h) compared with traditional Au/Ti-containing catalysts without adding promoters [26]. Further enhancing the activity by adding promoters (e.g., ionic liquid, metals) is also an interesting topic and will be carried out in our future study.

(Fig. 7 should be inserted here)

## **4** Conclusions

The intrinsic effect of Si/Ti molar on catalytic performance for propene epoxidation with H<sub>2</sub> and O<sub>2</sub> is examined on uncalcined TS-1 with blocked micropores (TS-1-B) supported Au catalyst, which makes it possible to accurately determine the activity and exclude the significant contribution of tiny Au clusters in the micropores. Results show that optimum value of the Si/Ti molar ratio is 40 for TS-1-B support. Lower Si/Ti molar ratio (e.g., 20) results in the existence of abundant extra-framework Ti species and thus promotes the non-selective epoxidation of propene. In addition, higher Si/Ti molar ratio is unfavorable because of the difficult transmission of hydroperoxide species from Au nanoparticle surface to the nearby Ti sites for epoxidation. The optimized 0.13 wt% Au/TS-1-B(40) catalyst shows high PO formation rate of 158  $g_{PO}h^{-1}kg_{Cat}^{-1}$  and PO selectivity of 83% at 200 °C over 30 h. It is hoped that the discovery will be beneficial to the design of highly active and selective Au/Ti-containing catalysts for propene epoxidation with H<sub>2</sub> and O<sub>2</sub>.

#### Acknowledgments

This work is financially supported by the Natural Science Foundation of China

(U1162112), the 111 Project of Ministry of Education of China (B08021).

#### References

[1] T. Hayashi, K. Tanaka, M. Haruta, Selective vapor-phase epoxidation of propylene over Au/TiO<sub>2</sub> catalysts in the presence of oxygen and hydrogen, J. Catal. 178 (1998) 566-575.

[2] J. Huang, T. Takei, T. Akita, H. Ohashi, M. Haruta, Gold clusters supported on alkaline treated TS-1 for highly efficient propene epoxidation with O<sub>2</sub> and H<sub>2</sub>, Appl. Catal. B 95 (2010) 430-438.

[3] W. Song, Y. Zuo, G. Xiong, X. Zhang, F. Jin, L. Liu, X. Wang, Transformation of SiO<sub>2</sub> in titanium silicalite-1/SiO<sub>2</sub> extrudates during tetrapropylammonium hydroxide treatment and improvement of catalytic properties for propylene epoxidation, Chem. Eng. J. 253 (2014) 464-471.

[4] G. Wu, Y. Wang, L. Wang, W. Feng, H. Shi, Y. Lin, T. Zhang, X. Jin, S. Wang, X. Wu, P. Yao, Epoxidation of propylene with H<sub>2</sub>O<sub>2</sub> catalyzed by supported TS-1 catalyst in a fixed-bed reactor: experiments and kinetics, Chem. Eng. J. 215-216 (2013) 306-314.

[5] M. Haruta, B.S. Uphade, S. Tsubota, A. Miyamoto, Selective oxidation of propylene over gold deposited on titanium-based oxides, Res. Chem. Intermed. 24 (1998) 329-336.

[6] C. Qi, T. Akita, M. Okumura, M. Haruta, Epoxidation of propylene over gold catalysts supported on non-porous silica, Appl. Catal. A 218 (2001) 81-89.

[7] J.J. Bravo-Suarez, K.K. Bando, J. Lu, M. Haruta, T. Fujitani, T. Oyama, Transient technique for identification of true reaction intermediates: hydroperoxide species in propylene epoxidation on gold/titanosilicate catalysts by X-ray absorption fine structure spectroscopy, J. Phys. Chem. C 112 (2008) 1115-1123.

[8] W.-S. Lee, M. Cem Akatay, E.A. Stach, F.H. Ribeiro, W. Nicholas Delgass, Enhanced reaction rate for gas-phase epoxidation of propylene using  $H_2/O_2$  by Cs promotion of Au/TS-1, J. Catal. 308 (2013) 98-113.

[9] X. Feng, X. Duan, G. Qian, X. Zhou, D. Chen, W. Yuan, Au nanoparticles deposited on the external surfaces of TS-1: enhanced stability and activity for direct propylene epoxidation with  $H_2$  and  $O_2$ , Appl. Catal. B 150-151 (2014) 396-401.

[10] X. Feng, X. Duan, G. Qian, X. Zhou, D. Chen, W. Yuan, Insights into size-dependent activity and active sites of Au nanoparticles supported on TS-1 for propene epoxidation with  $H_2$  and  $O_2$ , J. Catal. 317(2014) 99-104.

[11] W.-S. Lee, L.-C. Lai, M. Cem Akatay, E.A. Stach, F.H. Ribeiro, W.N. Delgass, Probing the gold

active sites in Au/TS-1 for gas-phase epoxidation of propylene in the presence of hydrogen and oxygen, J. Catal. 296 (2012) 31-42.

[12] L. Xu, Y. Ren, H. Wu, Y. Liu, Z. Wang, Y. Zhang, J. Xu, H. Peng, P. Wu, Core/shell-structured TS-1@mesoporous silica-supported Au nanoparticles for selective epoxidation of propylene with H<sub>2</sub> and O<sub>2</sub>, J. Mater. Chem. 21 (2011) 10852-10858.

[13] C. Qi, J. Huang, S. Bao, H. Su, T. Akita, M. Haruta, Switching of reactions between hydrogenation and epoxidation of propene over Au/Ti-based oxides in the presence of  $H_2$  and  $O_2$ , J. Catal. 281 (2011) 12-20.

[14] J. Huang, E. Lima, T. Akita, A. Guzmán, C. Qi, T. Takei, M. Haruta, Propene epoxidation with O<sub>2</sub> and H<sub>2</sub>: identification of the most active gold clusters, J. Catal. 278 (2011) 8-15.

[15] H. Yang, D. Tang, X. Lu, Y. Yuan, Superior performance of gold supported on titanium-containing hexagonal mesoporous molecular sieves for gas-phase epoxidation of propylene with use of  $H_2$  and  $O_2$ , J. Phys. Chem. C 113 (2009) 8186-8193.

[16] E. Sacaliuc, A.M. Beale, B.M. Weckhuysen, T.A. Nijhuis, Propene epoxidation over Au/Ti-SBA-15 catalysts, J. Catal. 248 (2007) 235-248.

[17] J. Lu, X. Zhang, J.J. Bravo-Suárez, K.K. Bando, T. Fujitani, S.T. Oyama, Direct propylene epoxidation over barium-promoted Au/Ti-TUD catalysts with H<sub>2</sub> and O<sub>2</sub>: effect of Au particle size, J. Catal. 250 (2007) 350-359.

[18] N. Yap, R.P. Andres, W.N. Delgass, Reactivity and stability of Au in and on TS-1 for epoxidation of propylene with  $H_2$  and  $O_2$ , J. Catal. 226 (2004) 156-170.

[19] A.K. Sinha, S. Seelan, S. Tsubota, M. Haruta, A three-dimensional mesoporous titanosilicate support for gold nanoparticles: vapor-phase epoxidation of propene with high conversion, Angew. Chem. Int. Ed. 43 (2004) 1546-1548.

[20] A.K. Sinha, S. Seelan, T. Akita, S. Tsubota, M. Haruta, Vapor phase propylene epoxidation over Au/Ti-MCM-41 catalysts prepared by different Ti incorporation modes, Appl. Catal. A 240 (2003) 243-252.

[21] B.S. Uphade, T. Akita, T. Nakamura, M. Haruta, Vapor-phase epoxidation of propene using  $H_2$  and  $O_2$  over Au/Ti-MCM-48, J. Catal. 209 (2002) 331-340.

[22] G. Mul, A. Zwijnenburg, B. van der Linden, M. Makkee, J.A. Moulijn, Stability and selectivity of Au/TiO<sub>2</sub> and Au/TiO<sub>2</sub>/SiO<sub>2</sub> catalysts in propene epoxidation: an in situ FT-IR study, J. Catal. 201 (2001) 128-137.

[23] M. Haruta, M. Daté, Advances in the catalysis of Au nanoparticles, Appl. Catal. A 222 (2001) 427-437.

[24] Y.-H. Yuan, X.-G. Zhou, W. Wu, Y.-R. Zhang, W.-K. Yuan, L. Luo, Propylene epoxidation in a microreactor with electric heating, Catal. Today 105 (2005) 544-550.

[25] G. Qian, Y.H. Yuan, W. Wu, X.G. Zhou, Vapor phase propylene epoxidation kinetics, Stud. Surf. Sci. Catal. 159 (2006) 333-336.

[26] W.-S. Lee, M. Cem Akatay, E.A. Stach, F.H. Ribeiro, W. Nicholas Delgass, Reproducible preparation of Au/TS-1 with high reaction rate for gas phase epoxidation of propylene, J. Catal. 287 (2012) 178-189.

[27] J. Lu, X. Zhang, J.J. Bravo-Suárez, T. Fujitani, S.T. Oyama, Effect of composition and promoters in Au/TS-1 catalysts for direct propylene epoxidation using H<sub>2</sub> and O<sub>2</sub>, Catal. Today 147 (2009) 186-195.

[28] B. Taylor, J. Lauterbach, W.N. Delgass, Gas-phase epoxidation of propylene over small gold

ensembles on TS-1, Appl. Catal. A 291 (2005) 188-198.

[29] C. Qi, T. Akita, M. Okumura, K. Kuraoka, M. Haruta, Effect of surface chemical properties and texture of mesoporous titanosilicates on direct vapor-phase epoxidation of propylene over Au catalysts at high reaction temperature, Appl. Catal. A 253 (2003) 75-89.

[30] M. Shekhar, J. Wang, W.-S. Lee, W.D. Williams, S.M. Kim, E.A. Stach, J.T. Miller, W.N. Delgass, F.H. Ribeiro, Size and support effects for the water-gas shift catalysis over gold nanoparticles supported on model Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub>, J. Am. Chem. Soc. 134 (2012) 4700-4708.

[31] W.D. Williams, M. Shekhar, W.-S. Lee, V. Kispersky, W.N. Delgass, F.H. Ribeiro, S.M. Kim, E.A. Stach, J.T. Miller, L.F. Allard, Metallic corner atoms in gold clusters supported on rutile are the dominant active site during water-gas shift catalysis, J. Am. Chem. Soc. 132 (2010) 14018-14020.

[32] W.-S. Lee, M. Cem Akatay, E.A. Stach, F.H. Ribeiro, W. Nicholas Delgass, Gas-phase epoxidation of propylene in the presence of  $H_2$  and  $O_2$  over small gold ensembles in uncalcined TS-1, J. Catal. 313 (2014) 104-112.

[33] X. Lu, G.-F. Zhao, Y. Lu, Propylene epoxidation with  $O_2$  and  $H_2$ : a high-performance Au/TS-1 catalyst prepared via deposition-precipitation using urea, Catal. Sci. Technol. 3 (2013) 2906-2909.

[34] L. Parker, D. Bibby, J. Patterson, Thermal decomposition of ZSM-5 and silicalite precursors, Zeolites 4 (1984) 168-174.

[35] X. Wang, X. Zhang, Y. Wang, H. Liu, J. Wang, J. Qiu, H. L. Ho, W. Han, K. L. Yeung, Preparation and performance of TS-1/SiO<sub>2</sub> egg-shell catalysts, Chem. Eng. J. 175 (2011) 408-416.

[36] P. Wu, T. Tatsumi, T. Komatsu, T. Yashima, A novel titanosilicate with MWW structure. I. hydrothermal synthesis, elimination of extraframework titanium, and characterizations, J. Phys. Chem. B 105 (2001) 2897-2905.

[37] Z. Wang, L. Xu, J.-g. Jiang, Y. Liu, M. He, P. Wu, One-pot synthesis of catalytically active and mechanically robust mesoporous TS-1 microspheres with the aid of triblock copolymer, Microporous Mesoporous Mater. 156 (2012) 106-114.

[38] E. Duprey, P. Beaunier, M.A. Springuel-Huet, F. Bozon-Verduraz, J. Fraissard, J.M. Manoli, J.M. Brégeault, Characterization of catalysts based on titanium silicalite, TS-1, by physicochemical techniques, J. Catal. 165 (1997) 22-32.

[39] D. Serrano, R. Sanz, P. Pizarro, I. Moreno, S. Medina, Hierarchical TS-1 zeolite as an efficient catalyst for oxidative desulphurization of hydrocarbon fractions, Appl. Catal. B 146 (2014) 35-42.

[40] R. Millini, E. Previde Massara, G. Perego, G. Bellussi, Framework composition of titanium silicalite-1, J. Catal. 137 (1992) 497-503.

[41] X. Wang, X. Zhang, H. Liu, J. Qiu, W. Han, K. L. Yeung, Investigation of Pd membrane reactors for one-step hydroxylation of benzene to phenol, Catal. Today 193 (2012) 151-157.

[42] Y. Guo, X. Wang, X. Zhang, Y. Wang, H. Liu, J. Wang, J. Qiu, K.L. Yeung, Pd-silicalite-1 composite membrane reactor for direct hydroxylation of benzene to phenol, Catal. Today 156 (2010) 282-287.

[43] J. Lu, X. Zhang, J.J. Bravo-Suárez, K.K. Bando, T. Fujitani, S.T. Oyama, Direct propylene epoxidation over barium-promoted Au/Ti-TUD catalysts with H<sub>2</sub>/O<sub>2</sub>: effect of Au particle size, J. Catal. 250 (2007) 350-359.

[44] J. Chen, S.J. Halin, E.A. Pidko, M. Verhoeven, D.M.P. Ferrandez, E.J. Hensen, J.C. Schouten, T.A. Nijhuis, Enhancement of catalyst performance in the direct propene epoxidation: A study into gold-titanium synergy, ChemCatChem 5 (2013) 467-478.

[45] M. Yang, L.F. Allard, M. Flytzani-Stephanopoulos, Atomically Dispersed Au-(OH)<sub>x</sub> Species

Bound on Titania Catalyze the Low-Temperature Water-Gas Shift Reaction, J. Am. Chem. Soc. 135 (2013) 3768-3771.

[46] E.E. Stangland, K.B. Stavens, R.P. Andres, W. Nicholas Delgass, Propylene epoxidation over gold-titania catalysts, Stud. Surf. Sci. Catal. 130 (2000) 827-832.

# Table captions:

**Table 1** Textural properties of TS-1-B supports with different Si/Ti molar ratios.

	Sample	Si/Ti molar ratio	$V_{MP^a} \left( cm^3 g^{\text{-}1} \right)$	$V_{P^{b}}(cm^{3}g^{-1})$	$S_{BET}\left(m^2g^{\text{-}1}\right)$	
-	TS-1-B(20)	20	0.01	0.04	9.1	•
	TS-1-B(40)	40	0.00	0.03	14.5	
	TS-1-B(50)	50	0.00	0.03	21.6	
	TS-1-B(90)	90	0.00	0.02	14.4	
	TS-1-B(100)	100	0.01	0.05	27.0	
	TS-1-B(150)	150	0.00	0.04	13.4	
	TS-1-B(200)	200	0.00	0.03	10.7	

Table 1 Textural properties of TS-1-B supports with different Si/Ti molar ratios.

 $^{a}$  Micropore volume  $\left( V_{MP}\right)$  is estimated by t-plot method.

<sup>b</sup> Pore volume (V<sub>P</sub>) is evaluated from the adsorption isotherm at the relative pressure about 0.99.

#### **Figure captions:**

**Fig. 1** XRD patterns of TS-1-B supports with different Si/Ti molar ratios of (a) 20, (b) 40, (c) 50, (d) 90, (e) 100, (f) 150 and (g) 200.

**Fig. 2** FT-IR spectra of TS-1-B supports with different Si/Ti molar ratios of (a) 20, (b) 40, (c) 50, (d) 90, (e) 100, (f) 150 and (g) 200.

**Fig. 3** UV-vis spectra of TS-1-B with different Si/Ti molar ratios of (a) 20, (b) 40, (c) 50, (d) 90, (e) 100, (f) 150 and (g) 200.

**Fig. 4** (a) PO formation rate, PO selectivity and (b) H<sub>2</sub> selectivity as a function of Si/Ti molar ratio.

**Fig. 5** Scheme of different reaction routes on Au/TS-1-B catalysts with (a) high and (b) low Si/Ti molar ratio.

**Fig. 6** PO formation rate and selectivity of Au/TS-1-B(40) catalysts as a function of Au loading.

**Fig. 7** PO formation rate of Au/TS-1-B and traditional Au/TS-1 catalysts as a function of time-on-stream.



**Fig. 1** XRD patterns of TS-1-B supports with different Si/Ti molar ratios of (a) 20, (b) 40, (c) 50, (d) 90, (e) 100, (f) 150 and (g) 200.



**Fig. 2** FT-IR spectra of TS-1-B supports with different Si/Ti molar ratios of (a) 20, (b) 40, (c) 50, (d) 90, (e) 100, (f) 150 and (g) 200.



**Fig. 3** UV-vis spectra of TS-1-B with different Si/Ti molar ratios of (a) 20, (b) 40, (c) 50, (d) 90, (e) 100, (f) 150 and (g) 200.



Fig. 4 (a) PO formation rate, PO selectivity and (b)  $H_2$  selectivity as a function of Si/Ti molar ratio.



**Fig. 5** Scheme of different reaction routes on Au/TS-1-B catalysts with (a) high and (b) low Si/Ti molar ratio.



**Fig. 6** PO formation rate and selectivity of Au/TS-1-B(40) catalysts as a function of Au loading.



**Fig. 7** PO formation rate of Au/TS-1-B and traditional Au/TS-1 catalysts as a function of time-on-stream.