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# Silylation enhances the performance of Au/Ti–SiO<sub>2</sub> catalysts in direct epoxidation of propene using $H_2$ and $O_2$



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# ABSTRACT

The effect of silylation on a series of Au/Ti-SiO<sub>2</sub> catalysts for the direct epoxidation of propylene in the presence of H<sub>2</sub> and O<sub>2</sub> was studied. It was found that silylation significantly improved catalyst performance: propylene conversion, propylene oxide (PO) selectivity, and H<sub>2</sub> efficiency increased. The extent of improvement depended on the Au and Ti content of the catalysts. The catalyst showing the best activity (Au(0.1)/Ti(1)–SiO<sub>2</sub>) exhibited an average PO formation rate of 121 g<sub>PO</sub> kg<sub>cat</sub><sup>-1</sup> h<sup>-1</sup> and a PO selectivity of 92% at 473 K, while the catalyst having the maximum Au and Ti loading (Au(1)/Ti(5)–SiO<sub>2</sub>) showed the most significant improvement in performance with a 78% increase in the rate of PO formation upon silylation. The catalysts were characterized by contact angle measurements, FTIR, TGA, TEM, ICP-OES and these observations were used to elucidate the key factors governing the enhanced catalytic performance upon silylation. It was found that the silylated catalyst exhibited superior performance due to increased hydrophobicity, which aids product desorption, a decrease in acidic sites that are responsible for side-product formation, and a possible redistribution of the Au particles.

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# 1. Introduction

The development of green catalytic processes will contribute greatly to the transition to a sustainable future. Particularly promising in this context are nanoscale catalysts, the compositions of which may be tailored to acquire desirable chemical properties. A coveted green catalytic process is the direct epoxidation of propene to propene oxide (PO) [1]. The development of this one-step green synthesis is important as traditional methods of PO production are either environmentally stressful (the chlorohydrin method) or have economic limitations (SM/PO and MTBE/PO both produce equal amounts of co-products) [2]. The more recent processes of PO production consist of multiple steps (the cumene hydroperoxide process by Sumitomo Chemicals) and use expensive oxidants (the HPPO process by Dow/BASF) [3], hence making the direct synthesis route highly relevant.

In an attempt to identify suitable catalysts for this desirable oxidation reaction, gold has taken the center of attention since the discovery by Haruta et al. [4] that gold on titania can produce PO in the presence of  $O_2$  and  $H_2$ . Several groups have demonstrated the possibility of propene epoxidation over catalysts comprising Au nanoparticles dispersed on Ti-containing supports such as TiO<sub>2</sub>, TiO<sub>2</sub>-SiO<sub>2</sub>, TS-1, Ti-MCM-41, Ti-MCM-48, Ti-SBA-15, and Ticontaining hydrophobic silsesquioxane [3,5]. The highest initial PO rates ( $\sim$ 300 g<sub>PO</sub> kg<sub>cat</sub><sup>-1</sup> h<sup>-1</sup>, 200 °C, GHSV = 14,000 mL g<sub>cat</sub><sup>-1</sup> h<sup>-1</sup>) have been reported by the group of Delgass on a Cs-promoted Au/TS-1 catalyst. The major drawback of this system is rapid catalyst deactivation [6]. Several attempts have been made to improve the stability of Au/TS-1, such as using uncalcined TS-1 to ensure that Au is deposited only on the external surface of the zeolite [7,8]. Chen et al. [9] have reported another active catalyst system, Au/Ti-SiO<sub>2</sub>, displaying stable PO reaction rates on the order of  $120 g_{PO} kg_{cat}^{-1} h^{-1}$  (200 °C, GHSV = 10,000 mL  $g_{cat}^{-1} h^{-1}$ ). Dispersing Au nanoparticles on Ti-grafted silica resulted in stabler catalyst performance with no significant deactivation on stream. Another benefit of this catalytic system is that in the gold deposition step,



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~100% gold is deposited on the support, which is not the case in the preparation of Au/TS-1 [8,10,11]. In the same work [9], it was also found that although low Au and Ti loadings led to highly active and stable Au/TiSiO<sub>2</sub> catalysts, they also formed relatively large amounts of propane, the formation of which could be suppressed to some extent by optimizing the Ti grafting procedure. Another report by the same authors described the addition of CO to the feed to suppress propene hydrogenation [12,13].

The reaction mechanism for PO formation that is most widely supported involves formation of a peroxy species, either in the form of OOH or  $H_2O_2$ , on small Au nanoparticles. These peroxy species spill over to preferably isolated tetrahedral Ti<sup>4+</sup> species. The resulting Ti-coordinated OOH/ $H_2O_2$  intermediate then oxidizes propene to PO and water [2,14,15]. Water is a by-product produced in larger quantities than the stoichiometric amount formed during epoxidation, which results from the direct combustion of  $H_2$ . This side reaction lowers the hydrogen efficiency of the process, which along with low propene conversion and poor catalyst stability has hindered commercialization of this process so far [1,2,16].

An attractive approach to improving the catalytic performance is to increase the hydrophobicity of the catalyst surface by silylation, a strategy that has been explored well for various titania-silica catalysts for different reactions. In the silvlation process, a silanol group of the support reacts with the alkylsilyl group of the silylating agent, thus rendering the material more hydrophobic. This in turn facilitates rapid desorption of polar products. Silylation can be carried out both in gas and liquid phases using different silylating agents [17-28]. Hydrophobization of Au-Ti catalysts for propene epoxidation was reported in patents by Weisbeck et al. [22], where hexamethyldisilazane was used as a silylating agent, and by Hayashi et al. [23], where trimethylmethoxysilane was found to be an effective silylating agent. Following this, Uphade et al. [24] reported that silylation using trimethylmethoxysilane (in the gas phase) led to increased PO selectivity, H<sub>2</sub> efficiency, and stability of the Au/Ti-MCM-48 catalyst. In another study [25], silvlation was carried out in the liquid phase using N-methyl-N-(trimethylsilyl)trifluoroacetamide (MSTFA) on Ti-MCM, and the resulting catalyst was found to have high PO selectivity even at higher operating temperatures, although there was no significant increase in the overall PO yield. There was also no improvement in terms of stability. Although there have been a few more studies [26–28], the effect of silvlation has not yet been investigated for the most recent and more active generation of Au-Ti catalysts for direct propene epoxidation. Furthermore, the influence of silvlation on factors other than surface hydrophobicity has not been elucidated yet. A final aspect, which warrants further investigation, is the effect of silylation on Au-Ti synergy.

In this work, we investigate in more detail the influence of silylation on the catalytic performance of Au/Ti-SiO<sub>2</sub> in direct propene epoxidation using H<sub>2</sub> and O<sub>2</sub>. Au/Ti-SiO<sub>2</sub> was chosen because of the excellent stability it exhibits, good shelf life, and high gold uptake in homogeneous deposition-precipitation. It is also one of the most active Au-Ti catalysts reported to date, with a stable rate of PO formation >100  $g_{PO} kg_{cat}^{-1} h^{-1}$  at 473 K [9,16]. Earlier, it was found that prolonged grafting of Ti resulted in decreased propane side-product formation. Here, we show that longer grafting can completely suppress propene hydrogenation. We use this grafting procedure to synthesize supports with different Ti coverage of the silica surface (0.5, 1, and 5% monolayer Ti), followed by Au deposition (0.05, 0.1, and 1 wt.%). Thereafter, all the catalysts were subjected to the silvlation treatment in order to study its effect on the propene epoxidation performance. The Ti coordination in the Ti-SiO<sub>2</sub> was investigated by DR-UV-vis spectroscopy. Characterization of optimum catalysts further included contact-angle measurements, TGA, FTIR, and TEM techniques.

## 2. Experimental

#### 2.1. Catalyst synthesis

As support, we employed silica to which Ti was grafted according to a known procedure [9]. In a typical synthesis, as-received silica (15 g, Davisil-643, 300 m<sup>2</sup>/g, average pore size 150 Å, pore volume 1.15 cm<sup>3</sup>/g) was dried and suspended in 250 mL anhydrous 2-propanol (Aldrich, 99%) under N<sub>2</sub> in a glove box. The resulting suspension was stirred for 10 min, after which tetraethylorthotitanate (TEOT, Aldrich, 97%) was added in such an amount that the Ti coverage was 0.5, 1, or 5% of the monolayer coverage of the silica. Based on the hydroxyl content of the silica, a loading of 1 wt.% Ti corresponds to 5% monolayer coverage. After the slurry had been stirred for 30 min, 2-propanol was slowly evaporated using a rotary evaporator at 328 K and 100 mbar. Evaporation of the solvent took around 4 h. The powder obtained was dried overnight at 353 K, followed by calcination at 393 K (heating rate 5 K/ min, isothermal period 2 h) and 873 K (heating rate 10 K/min, isothermal period 4 h). Gold was deposited on Ti-SiO<sub>2</sub> using a de position-precipitation method described by Chen et al. [9]. The support (2 g) was dispersed in 100 ml ultrapure water (18.2 M $\Omega$  cm at 25 °C). The pH was adjusted to ~9.5 using a 2.5 wt.% ammonia solution. The desired amount of HAuCl<sub>4</sub> (Aldrich, 30 wt.% in HCl) was diluted in 20 ml water, and was then added dropwise using a burette in ca. 15 min. Thereafter, the slurry was kept stirring for 1 h, while the pH was maintained at 9.4-9.5 by adding ammonia dropwise. The solid was collected by filtration and washed three times using deionized water. The catalyst was dried overnight at 353 K and calcined at 393 K (heating rate 5 K/ min, isothermal period 2 h) and 673 K (heating 10 K/min, isothermal period 4 h) in static air. The catalysts are denoted as Au(x)/Ti(y)–SiO<sub>2</sub>, where x is the nominal Au loading (in wt.%) and y is the percentage monolayer coverage.

For silylation, vapors of methoxytrimethylsilane were passed through the catalyst bed, which was maintained at 423 K for 15–30 min. This was done by bubbling Ar through a saturator containing methoxytrimethylsilane, which was kept at 298 K. This was followed by flushing with Ar at 473 K for 5 h [28]. The silylated catalysts are denoted by the suffix "Sil."

## 2.2. Catalyst characterization

The coordination state of Ti was determined by diffuse reflectance UV–vis (DR-UV–vis) spectra using a Shimadzu UV-2401PC spectrometer with  $BaSO_4$  serving as the reference.

The Ti and Au content of the catalysts was analyzed by inductively coupled plasma optical emission spectroscopy (ICP-OES) in a SpectroCiros CCD spectrometer. First aqua regia was added to the samples, and then this mixture was heated under stirring for 30 min. The solutions were cooled and then dilute HF (1:15 by volume in water) was added and the solution was swirled until clear.

Transmission electron microscopy (TEM) was used to determine the size of the Au nanoparticles. Sample preparation involved sonication of the samples in pure ethanol and application of a few droplets of the suspension to a 200 mesh Cu TEM grid with a holey carbon support film. TEM micrographs were acquired on an FEI Tecnai 20 transmission electron microscope at an acceleration voltage of 200 kV with a LaB<sub>6</sub> filament. TEM images were recorded at different magnifications using a Gatan 1 k × 1 k CCD camera. Particle size and distribution were obtained by measuring at least 250 nanoparticles for each sample.

The hydrophobicity of the silylated catalyst was measured using a goniometer (Dataphysics OCA 30). The catalyst sample was pressed into a wafer and a drop of water ( $\sim$ 8 µL) was placed

on its surface using a needle. Images clearly showing the liquidsolid interface were collected and left and right contact angles were measured using the Dataphysics software. The TG-DTG data profiles were measured using Mettler Toledo TGA/DSC.

Infrared spectra were recorded on a Bruker Vertex 70v apparatus. The samples were pressed into self-supporting discs ( $\sim$ 10 mg weight) and placed in the IR cell. The samples were degassed at 423 K for 1 h and spectra were recorded at 323 K. For pyridine FTIR measurements, the same setup was used and pyridine vapors were passed over the catalyst wafer at 423 K for 1 h. Spectra were recorded at 423 K following desorption for 1 h at 473 K and 623 K.

## 2.3. Catalytic activity measurements

Catalytic activity measurements were performed in a flow setup equipped with an Interscience gas chromatography system (analysis time ~5 min) containing two analysis channels equipped with Porabond Q and Molsieve 5A columns and thermal conductivity detectors. The catalyst was loaded in a quartz reactor tube, which was placed in a tubular oven. A typical reaction cycle was 5 h followed by a regeneration step at 573 K with 10 vol% O<sub>2</sub> in He for 1 h. In a typical test, 150 mg of catalyst was loaded into the reactor, and the total flow was adjusted to 25 ml/min (GHSV = 10,000 ml  $g_{cat}^{-1}$  h<sup>-1</sup>). Reaction cycles were carried out typically in the temperature range 423–493 K. The rate of each catalytic cycle was calculated as the average of the rates between 150 and 300 min on stream.

The propene conversion (*X*) and selectivity to different products ( $S_x$ , where *x* denotes the product) were calculated for the reaction  $nC_3H_6 \rightarrow mC_x$  and expressed as

$$X \ (\%) = \frac{\sum \frac{n}{m} P_x}{P_{C_3 H_6}^{\text{out}} + \sum \frac{n}{m} P_x} \times 100 = \frac{\sum \frac{n}{m} P_x}{P_{C_3 H_6}^{\text{in}}} \times 100,$$
(1)

$$S_x (\%) = \frac{\frac{n}{m} P_x}{\sum \frac{n}{m} P_x} \times 100, \tag{2}$$

where  $P_x$  is the partial pressure of the carbon-containing products obtained during the epoxidation of propene (PO, acrolein, acetone, propanal, acetaldehyde, and CO<sub>2</sub>) and the terms  $P_{C_3H_6}^{in}$  and  $P_{C_3H_6}^{out}$  denote the propene concentrations at the inlet and outlet of the reactor respectively; and

$$\eta_{\rm H2} \ (\%) = \frac{r_{\rm PO}}{r_{\rm PO} + r_{\rm H2O}} \times 100, \tag{3}$$

where  $r_{\rm PO}$  and  $r_{\rm H2O}$  are the rates of PO and water formation, respectively.

The absence of mass transfer limitations was verified using the Weisz–Prater criterion ( $C_{WP} < 1$ ) and the Mears criterion ( $C_M < 0.15$ ) for internal and external mass transfer limitations, respectively.  $C_{WP}$  was found to be on the order of  $10^{-6}$  ( $\ll 1$ ) and  $C_M$  on the order of  $10^{-6}$  ( $\ll 0.15$ ), thus ensuring that the system was free of mass transfer limitations (see Supporting Information).

## 3. Results and discussion

### 3.1. Support characterization

Grafting of TEOT onto the silica surface resulted in three different Ti–SiO<sub>2</sub> supports. Elemental analysis showed that the Ti loadings (percentile monolayer coverage between brackets) were 0.1 wt.% (0.5% ML), 0.21 wt.% (1% ML), and 0.88 wt.% (5% ML) Ti for Ti(0.5)–SiO<sub>2</sub>, Ti(1)–SiO<sub>2</sub>, and Ti(5)–SiO<sub>2</sub>, respectively. Fig. 1 shows the diffuse reflectance UV–vis spectra of the three supports used in this study. The relatively narrow band around 210 nm for Ti(0.5)–SiO<sub>2</sub>–0.5 and Ti(1)–SiO<sub>2</sub> points to the high dispersion of Ti on the silica surface as isolated tetrahedral species. Ti(5)–SiO<sub>2</sub>,



Fig. 1. DR-UV-vis spectra of the three different supports having Ti monolayer coverage of 0.5% (solid line), 1% (dashed-dotted line), and 5% (dashed line).

on the other hand, also contains Ti species in higher coordination, in isolated form and as agglomerated species [9,29,30].

## 3.2. Effect of silylation on activity

Gold was deposited at different loadings on these Ti-modified supports by homogeneous deposition–precipitation. After calcination, an aliquot of each sample was silylated. Before discussing in more detail the effect of silylation on the various Au–Ti catalysts, we first report its influence on the catalytic performance for Au (0.1)/Ti(1)–SiO<sub>2</sub>. Fig. 2 shows the reaction rates of PO and water for the parent and the silylated sample at 473 K. The absence of deactivation with time on stream is in line with earlier reported data for propene oxidation on similar Au–Ti catalysts [5,9,16]. The silylated catalyst displays stable performance with time on stream and shows a higher PO reaction rate than that on the unsilylated one, as evident from Fig. 2a. A smaller amount of water produced after silylation, as shown in Fig. 2b, results in higher H<sub>2</sub> efficiency of the silylated catalyst.

We observe that the silylated sample shows activation behavior during subsequent activity-regeneration cycles. This feature was not observed for the parent (nonsilylated) sample. This is highlighted in Fig. 3 for Au(0.1)/Ti(1)–SiO<sub>2</sub>–Sil, in which reaction rates for a period of 5 h are presented at temperatures of 473-453-493-473 K, with intermittent oxidative regeneration at 573 K. In the first cycle (473 K), the amount of PO formed increases with time. In the fourth cycle (473 K), the PO formation is higher and nearly stable. Subsequent cycles under similar conditions lead to nearly similar stable activity (not shown). The initial low activity of a silylated catalyst has also been reported in a previous study [24]. To gain insight into the cause of this activation behavior, we studied various catalysts with CO-FTIR. It is found that calcination of the silvlated sample leads to an increase of a CO band due to interaction with Ti<sup>4+</sup>. We speculate that silylation of Lewis acid Ti sites, essential in the mechanism of PO oxidation involving OOH/H<sub>2</sub>O<sub>2</sub> intermediates, is blocked during silvlation. Calcination slowly removes the species that block these active sites, so that the increased activity can be explained as a function of reaction-regeneration (Supporting Information).



**Fig. 2.** Time-on-stream formation rate of (a) PO and (b) water during a 5 h catalytic test over Au(0.1)/Ti(1)–SiO<sub>2</sub> (black squares) and Au(0.1)/Ti(1)–SiO<sub>2</sub>–Sil (red circles) catalysts at 473 K,  $H_2/O_2/C_3H_6/He = 1:1:1:7$ , GHSV = 10,000 mL  $g_{cat}^{-1}$  h<sup>-1</sup>.



**Fig. 3.** Rate of formation of PO on Au(0.1)/Ti(1)–SiO<sub>2</sub>–Sil at different reaction temperatures at conditions  $H_2/O_2/C_3H_6/He$  = 1:1:1:7 and GHSV = 10,000 mL  $g_{cat}^{-1}h^{-1}$ .

### 3.3. Characterization of silylated catalyst

We then investigated the influence of the silylation treatment on the catalytic surface. It is expected that silylation will render the surface more hydrophobic. It should be noted that silylation was carried out on the Au-containing samples, as previous work [24] showed that this was more beneficial than loading gold onto a silylated sample. This is reasonable, as the absence of hydroxyl groups would otherwise lower the gold dispersion. The high hydrophilicity of the surface of Au(0.1)/Ti(1)–SiO<sub>2</sub> follows from the contact angle of ~5°. After silylation, the contact angle increased to ~31°, showing that silylation strongly increased the hydrophobicity of the surface (Supporting Information).

Fig. 4 shows TGA curves for the parent and the silylated Au(0.1)/Ti(1)–SiO<sub>2</sub>. Before heating, the samples were kept in saturated water vapor for 1 h at room temperature. The weight loss up to 430 K is mainly due to associated water [41], and is observed to be lower in the silylated sample. Hence, the TGA curves demonstrate that silylation increases the hydrophobicity of the sample, which is in agreement with the contact angle measurements reported above. Another significant difference, indicated by TGA, is the absence of the feature due to dehydroxylation (condensation of silanol groups) around 623 K in the silylated sample, which



Fig. 4. TG profiles of Au(0.1)/Ti(1)–SiO<sub>2</sub> (solid line) and Au(0.1)/Ti(1)–SiO<sub>2</sub>–Sil (dashed–dotted line) from 323 to 1023 K.

shows that silanol groups have been converted. This will be confirmed by FTIR spectroscopy.

We also investigated by IR spectroscopy the changes brought about by silylation and activation of the catalyst in oxygen at 523 and 573 K. For this purpose, the parent and silylated Au(0.1)/Ti(1)-SiO<sub>2</sub> samples were evacuated in the environmental cell at 423 K for 1 h. IR spectra were recorded at 323 K. Fig. 5a shows that these spectra contain bands at 3743 cm<sup>-1</sup> due to isolated silanol groups and a broad band centered around 3555 cm<sup>-1</sup> corresponding to hydrogen-bonded silanols and associated water [20,25]. The difference spectra before and after silvlation (Fig. 5b) clearly show the decreased intensity of isolated silanol groups. Comparatively, the changes in hydrogen-bonded silanol groups and associated water are less pronounced. The peaks at 2964 and 2905  $cm^{-1}$ (see inset of Fig. 5a) are due to trimethylsilyl groups on the silica surface [41,21,42]. All samples including the nonsilylated one contain additional C-H vibrations, which, in case of the unsilylated sample (peak at 2928 cm<sup>-1</sup>), can be attributed to residual ethoxy groups from the TEOT precursor used during Ti grafting. On the other hand, the additional peak at 2857 cm<sup>-1</sup> observed in the silylated sample can be assigned to methoxy groups, which may be formed due to the reaction of the methanol (the by-product of silylation) with silanols or siloxane bridges. A similar observation was made when trimethylethoxysilane was used as a silylating agent on Ti-MCM-41 and additional bands due to ethoxy groups were observed [21]. The reaction of the silylating agent trimethyl2964



**Fig. 5.** (a) IR Spectra of Au(0.1)/Ti(1)–SiO<sub>2</sub> (i) unsilylated, (ii) silylated, (iii) silylated and treated in O<sub>2</sub> for 30 min at 523 K followed by (iv) treatment at 573 K in O<sub>2</sub> for 30 min. Inset: features between 3000 and 2800 cm<sup>-1</sup>. (b) Difference spectrum (ii)–(i) showing the changes after silylation. (c) Difference spectrum (iv)–(ii) showing the changes of silylated sample before and after treatment at 573 K in O<sub>2</sub>.

methoxysilane (TMMS) with silanols and siloxane bridges is shown in Scheme 1, along with possible side reactions of methanol from surface silylation.

Calcination of the silylated samples at 523 and 573 K in oxygen did not profoundly affect the C–H bands in the silylated samples, as seen in the difference spectra, Fig. 5c, except for the erosion of the 2928 cm<sup>-1</sup> band and the decrease in the 2857 cm<sup>-1</sup> band. This suggests that the oxidation treatment results in further conversion of residual alkoxy groups. Fig. 5c also shows that this treatment led to significant decrease of the broad band around 3555 cm<sup>-1</sup>, with a simultaneous increase in the number of isolated silanols

(3743 cm<sup>-1</sup>). These changes can be attributed to the dehydroxylation of the hydrogen-bonded silanols, yielding siloxane bridges and silanols as shown in Scheme 2.

## 3.4. Catalytic performance: Influence of Au and Ti loading

We then investigated the influence of Au and Ti loading on catalytic performance before and after silylation. The resulting performance data are provided in Table 1 for comparison. The variation in Au and Ti loading has a considerable effect on the performance of the parent (nonsilylated) catalysts. First we observe that these



Scheme 1. Reaction of silylating agent trimethylmethoxysilane (TMMS) with (i) silanols and (ii) siloxane bridges, and probable reactions of methanol side product with (iii) silanols and (iv) siloxane bridges.



Scheme 2. Dehydroxylation of hydrogen-bonded silanols to form siloxane bridges and silanols.

samples do not produce propane, which was the case in a previous study [9]. This could be achieved by prolonging the Ti grafting time, which resulted in a decrease of propene hydrogenation to propane (Supporting Information). The data also reveal that the samples with predominantly isolated tetrahedral Ti atoms (Au (0.05)/Ti(0.5)–SiO<sub>2</sub> and Au(0.05)/Ti(1)–SiO<sub>2</sub>) show much higher activity than the sample containing agglomerated Ti (Au(0.05)/Ti (5)–SiO<sub>2</sub>. The lower activity of Au(1)/Ti(5)–SiO<sub>2</sub> is likely due to the decreased number of isolated tetrahedral Ti atoms, which lowers the selectivity toward PO and hence the total PO formation [9,34,36]. The highest PO formation rate is observed for the catalyst Au(0.1)/Ti(1)–SiO<sub>2</sub> with  $r_{PO} \sim 107 \text{ g}_{PO} \text{ h}^{-1} \text{ kg}_{cat}^{-1}$ , a PO selectivity of 90%, and a H<sub>2</sub> efficiency of 12%. The overall trends observed are in keeping with insights from the literature [9].

Comparing these performances with data for the silylated catalysts, we observe that the propene conversion increases and the CO2 selectivity decreases in all cases. This is reasonable, as the more hydrophobic reaction environment should decrease the residence time of PO on the surface and, accordingly, its propensity toward decomposition. For most of the catalysts, we also observe an increase in the PO selectivity, except for  $Au(1)/Ti(0.5)-SiO_2$ . In this case, silvlation leads to decreased PO selectivity (from 80% to 72%) and increased acrolein selectivity (from 7% to 11%). The best performance upon silvlation is obtained for Au(0.1)/Ti(1)-SiO<sub>2</sub>-Sil with  $r_{PO} = 121 \text{ g}_{PO} \text{ kg}_{cat}^{-1} \text{ h}^{-1}$  at a PO selectivity of 92% and a H<sub>2</sub> efficiency of 14%. The greatest improvement in activity upon silylation is observed for Au(1)/Ti(5)-SiO<sub>2</sub>, where the rate of PO production increases from 41 to 73  $g_{PO} kg_{cat}^{-1} h^{-1}$  and the selectivity to PO increases from 74 to 82%, while the conversion increases from 3.4 to 5.3%. From Table 1, it is also observed that the performance enhancement upon silvlation is not the same at all Ti and Au loadings.

#### Table 1

Performance of silylated and unsilylated catalysts.<sup>a</sup>

Catalyst	Au loading, wt.% Nominal (Real <sup>b</sup> )	Ti loading, wt.% Nominal (Real <sup>b</sup> )	Conversion (%)	Selectivity (%)						H <sub>2</sub> efficiency,	r <sub>PO</sub>
				РО	Acetaldehyde	Acetone	Propanal	Acrolein	CO <sub>2</sub>	η <sub>H2</sub> (%) <sup>c</sup>	$(g_{PO} kg cat h^{-1} h^{-1})$
Au(0.05)/Ti(0.5)–SiO <sub>2</sub> Au(0.05)/Ti(0.5)–SiO <sub>2</sub> –Sil	0.05 (0.07)	0.1 (0.1)	1.8 2.6	87.6 92.5	1.1 1.2	4.0 2.4	2.3 1.7	4.9 2.2	0.08 0.06	8 12	43 66
$Au(1)/Ti(0.5)-SiO_2^d$ $Au(1)/Ti(0.5)-SiO_{2-}-SiI^d$	1.0 (0.76)		1.7 1.9	79.9 71.9	2.8 4.2	5.7 5.8	2.5 3.2	6.7 10.6	2.4 1.1	3 3	38 38
Au(0.05)/Ti(1)–SiO <sub>2</sub> Au(0.05)/Ti(1)–SiO <sub>2</sub> –Sil	0.05 (0.07)	0.2 (0.21)	2.3 3.2	84.6 90.3	0.2 0	6.2 2.8	5.6 3.6	2.9 3.0	0.3 0.2	11 17	49 71
Au(0.1)/Ti(1)-SiO <sub>2</sub> Au(0.1)/Ti(1)-SiO <sub>2</sub> -Sil	0.1 (0.11)		4.5 4.8	89.5 91.9	1.3 1.3	3.4 2.4	2.2 2.4	2.2 1.3	1.4 0.8	12 14	107 121
$\begin{array}{l} \operatorname{Au(1)/Ti(1)-SiO_2}^d\\ \operatorname{Au(1)/Ti(1)-SiO_2-Sil^d} \end{array}$	1.0 (0.75)		4.4 4.6	82 81.4	0.2 0.2	5.3 5.6	0.1 0.1	7.0 7.5	5.4 5.2	4 4	82 84
Au(0.05)/Ti(5)–SiO <sub>2</sub> Au(0.05)/Ti(5)–SiO <sub>2</sub> –Sil	0.05 (0.07)	1.0 (0.88)	0.9 1.0	65.9 86.3	1.7 1.2	12.0 2.0	13.6 6.3	6.8 4.2	0 0	9 17	16 25
Au(1)/Ti(5)–SiO <sub>2</sub> <sup>e</sup> Au(1)/Ti(5)–SiO <sub>2</sub> –Sil <sup>e</sup>	1.0 (0.5)		3.4 5.3	74.0 82.2	1.8 2.0	6.8 3.4	8.4 5.2	3.9 3.6	5.0 3.7	7 10	41 73

<sup>a</sup> Reaction conditions:  $H_2/O_2/C_3H_6/He = 1:1:1:7$ , GHSV = 10,000 mL  $g_{cat}^{-1}h^{-1}$  at 473 K unless mentioned otherwise.

<sup>6</sup> Reaction continuous:  $H_{2}/O_{2}/C_{3}H_{6}/F$ <sup>6</sup> As found by ICP-OES. <sup>6</sup> H<sub>2</sub> Efficiency (%) =  $\frac{r_{00}}{r_{10} + r_{120}} \times 100$ . <sup>d</sup> Reaction performed at 423 K. <sup>e</sup> Reaction performed at 453 K.





Fig. 6. TEM images of (a) Au(0.1)/Ti(1)-SiO<sub>2</sub> and (b) Au(0.1)/Ti(1)-SiO<sub>2</sub>-1-Sil along with the corresponding particle size distributions; also shown is the distribution for the corresponding spent sample.



Fig. 7. TEM images of (a) Au(1)/Ti(5)-SiO<sub>2</sub> and (b) Au(1)/Ti(5)-SiO<sub>2</sub>-Sil, along with the corresponding particle size distributions.

# 3.5. Effect of silylation on particle size and acidity

To explain the activity trends observed upon silylation, we characterized selected silylated and unsilylated catalysts in more detail. Fig. 6 shows representative TEM images of the parent Au (0.1)/Ti(1)-SiO<sub>2</sub> catalyst and its silvlated counterpart along with the corresponding gold particle size distributions. The parent sample contains a range of gold nanoparticles ranging from just below 1 nm to about 3-5 nm. The average particle size is  $1.6 \pm 0.9$  nm. Upon silvlation, the particle size distribution changed, in the sense that particles larger than 2.5 nm were nearly absent. The average particle size of the silvlated catalyst is  $1.1 \pm 0.4$  nm, slightly lower than that in the fresh catalyst. This may indicate that silvlation of the Au/Ti-SiO<sub>2</sub> sample results in redistribution of gold over the surface. We also analyzed the spent catalyst in the same way. Typically, it is seen that the average particle size increased only slightly and, in particular, no particles larger than 3 nm were observed in the silvlated catalysts, which contrasted with the particles seen for the fresh catalysts.

The particle redistribution argument was further investigated for Au(1)/Ti(5)–SiO<sub>2</sub>, as this sample showed the greatest improvement upon silylation. The results are shown in Fig. 7 and further support the finding that gold particles appear to redisperse during the silylation treatment. The nonsilylated catalyst contains particles larger than 6 nm, while these are absent in the silylated catalyst. Moreover, the particle size distribution is narrower after silylation. This, in turn, also leads to a decrease in the average particle size, as indicated in Fig. 7.

To investigate whether silylation led to any change in the acidic properties of the catalyst, pyridine FTIR was carried out on parent and silylated Au(1)/Ti(5)–SiO<sub>2</sub> samples. We investigated this sample because silylation affected its performance the most among all catalysts. Fig. 8 shows that silylation results in a decrease of the amount of Brønsted acid sites as followed from the lower intensity of the 1637, 1545, and 1490 cm<sup>-1</sup> bands [32,33]. Brønsted acidity in these samples is assumed to originate from Ti–O–Si bridges, with Ti being in penta- or hexacoordination as in TiO<sub>x</sub> aggregates rather than in tetrahedral coordination [31,34]. These sites are



**Fig. 8.** Pyridine FTIR of Au(1)/Ti(5)-SiO<sub>2</sub> (black line) and Au(1)/Ti(5)-SiO<sub>2</sub>-Sil (red line). L: peak assigned to Lewis acid sites; B: peak assigned to Brønsted acid sites.



**Scheme 3.** Schematic diagram showing epoxidation on (a) unsilylated catalyst and (b) silylated catalyst. Au: gold nanoparticles; Ti<sub>ep</sub>: Ti sites active for epoxidation; Ti<sub>a</sub>: acidic Ti sites. PO forms at the Au–Ti<sub>ep</sub> interface; the water formation along with PO is not shown, for simplicity.

likely responsible for the formation of bidentate propoxy species from PO, which gives rise to such undesired side-products as propanal and acetone [34–37]. Silylation converts these acidic groups into (inactive) Si–O–Ti (CH<sub>3</sub>)<sub>3</sub> moieties, explaining the decreased Brønsted acidity. This leads to an increase in the selectivity to PO, as shown above.

#### 3.6. General discussion

Au/Ti–SiO<sub>2</sub> is reported to be an efficient catalyst for the hydroepoxidation of propene [9,12,13,16,40]. Its ease of preparation, high activity, and stability on stream, along with facile regeneration, make this a promising catalyst for future application in industry. Major drawbacks are undesired propane formation, low propene conversion, and low H<sub>2</sub> efficiency [9]. In this study, an attempt was made to address these shortcomings. While support preparation was optimized to suppress propene hydrogenation, silylation was employed to further enhance catalyst performance.

It has been proposed that certain TiO<sub>x</sub> species contribute to propane formation in Ti–SiO<sub>2</sub> supported gold catalysts [9]. The time of Ti grafting affected the dispersion and coordination state of Ti. Careful optimization of the Ti grafting procedure led to highly dispersed Ti on silica and complete suppression of propane formation. Further optimization of Au and Ti content was carried out and Au (0.1)/Ti(1)–SiO<sub>2</sub> was identified to be the best-performing catalyst, with a rate of PO formation of 107 g<sub>PO</sub> kg<sub>cat</sub><sup>-1</sup> h<sup>-1</sup>. PO selectivity of 90%, and  $\eta_{H2}$  = 12% at 473 K (GHSV = 10,000 mL g<sub>cat</sub><sup>-1</sup> h<sup>-1</sup>). The effect of gas phase silylation using TMMS was then studied on this catalyst and a further enhancement of performance was observed (Table 1). This encouraged us to study the effect of silylation on a series of Au–Ti catalysts with the aim of gaining insight into the main effect of silylation on the catalyst.

First, we verified the effectiveness of silylation by contact angle and TGA measurements. Contact angle measurements showed that silylation increased the hydrophobicity of the catalyst. This was also evident from TGA, where the weight loss due to water was found to be smaller for the silylated sample. Further characterization included IR spectroscopy, where it was found that there were fewer isolated silanols in the silylated sample, along with the presence of signature peaks of trimethylsilyl groups, indicating successful silylation. The retention of these peaks, when subjected to high temperatures and  $O_2$  flow, indicated that the silyl groups were not lost under reaction and regeneration conditions.

Further characterization revealed that silylation also led to a decrease in the number of Brønsted acid sites of the catalyst (pyridine FTIR) and also hinted at possible redistribution of large Au particles into smaller ones (TEM), the mechanism of which needs further systematic investigation. So in summary, the effect of silylation on the catalyst was found to be threefold: an increase of surface hydrophobicity, a decrease in the number of Brønsted acid sites, and an increase in Au dispersion. These three factors will be used next to explain the catalytic activity trends observed for the silylated catalysts at different Au and Ti content.

- From the catalytic activity results, we observed that most of the catalysts showed *activation* behavior during the reaction before reaching their optimum performance. CO FTIR measurements show that this is due to blocking of active Au–Ti sites by the silylating agent, which was slowly removed in situ during the reaction. After several reaction–regeneration cycles, the catalysts attained their final and stable activity.
- 2. Performance results showed that the influence of silylation was highly dependent on Au and Ti loading. The maximum rate of PO production was obtained for Au(0.1)/Ti(1)–SiO<sub>2</sub>–Sil, while the maximum improvement due to silylation was observed for Au(1)/Ti(5)–SiO<sub>2</sub>. It was observed that there was a significant improvement in performance at lower Au loadings for all the supports. This was reflected by increases in propene conversion, PO selectivity, rate of formation of PO, and H<sub>2</sub> efficiency. On the other hand, at higher Au loadings, the trend was somewhat different. For the catalyst with lowest Ti loading (Au(1)/Ti (0.5)–SiO<sub>2</sub>–Sil), there was, in fact, a decrease in PO rate and selectivity; at intermediate Ti loadings (Au(1)/Ti(1)–SiO<sub>2</sub>–Sil) there was only a slight improvement in performance; for the

highest Ti-containing catalyst  $(Au(1)/Ti(5)-SiO_2-SiI)$ , the improvement is most significant, as mentioned earlier. We explain these trends as follows:

- At low Ti content and sufficiently high Au loading (Au(1)/Ti (0.5)–SiO<sub>2</sub>), the catalyst contains significant numbers of Au nanoparticles in contact with pure silica. Au/SiO<sub>2</sub> exhibits negligible PO formation, as opposed to Au in contact with Ti sites during propene epoxidation. Instead, it has been found that Au/SiO<sub>2</sub> produces mainly acrolein and acetalde-hyde during propene oxidation [38,39]. In this particular catalyst, the redispersion of Au has a negative effect, as it will lead to an increasing fraction of Au nanoparticles in contact with silica rather than with the few isolated Ti sites. This seems to be in line with the increased selectivity toward acrolein and acetaldehyde, as observed in the performance data.
- At high Ti content (5% ML), the surface is characterized by the presence of agglomerated forms of titania as well as Brønsted acid sites, as evident from pyridine FTIR measurements. Earlier studies have shown that PO adsorbs strongly on both Si–OH and Ti–OH sites [34–37]. The resulting bidentate propoxy groups can react further to propanol and acetone, which are side-products of propene epoxidation [34]. The main effect of silylation is to deactivate these acidic sites. Although observed for most of the catalysts, increased PO selectivity is most pronounced for the catalysts with the highest Ti loading (Au(0.05)/Ti(5)–SiO<sub>2</sub>–Sil and Au(1)/Ti(5)– SiO<sub>2</sub>–Sil). This is likely because this catalyst contains the largest number of penta/hexa-coordinated Ti sites, which were successfully deactivated by silylation.

Accordingly, the present data show that along with increased hydrophobicity, other factors such as change in acidity and redistribution of Au particles play key roles in determining the catalyst activity after silylation. Scheme 3 schematically depicts how silylation improves the catalytic performance of Au/Ti–SiO<sub>2</sub> in the direct epoxidation of propene. In case of the unsilylated catalyst (Scheme 3a), once PO is formed, it is strongly adsorbed onto neighboring silanol and titanol acidic sites. While the PO adsorbed on the silanol is subsequently removed, that adsorbed on the acidic Ti site forms bidentate species and subsequently contributes to side-products that lower PO selectivity. On the other hand, in case of the silylated catalyst (Scheme 3b), the PO formed is readily desorbed from the catalyst surface, as the silanols and the acidic Ti sites are unreactive due to silylation. This in turn facilitates increasing propene conversion as well as PO selectivity.

## 4. Conclusions

The present study shows that silvlation can lead to significant improvement in the performance of Au/Ti-SiO<sub>2</sub> for the direct epoxidation of propene using H<sub>2</sub> and O<sub>2</sub>. A series of Au/Ti-SiO<sub>2</sub> catalysts having different Au-Ti content were studied before and after silylation. In all cases, silylation was successfully carried out in the gas phase using trimethylmethoxysilane after Au deposition and calcination. It was found that the extent of improvement of catalytic activity upon silvlation is largely governed by the Au and Ti content. It is proposed that silvlation leads to the formation of Si-O-Si (CH<sub>3</sub>)<sub>3</sub> and Ti–O–Si (CH<sub>3</sub>)<sub>3</sub> moieties, which not only increase the hydrophobicity but also decrease the acidity of the catalyst. This study further revealed that the redistribution of Au nanoparticles may play an additional role in determining the catalytic activity after silvlation. The most active silvlated catalyst showed a stable rate of PO formation of  ${\sim}121\,g_{PO}\,kg_{cat}^{-1}\,h^{-1}$  with PO selectivity 92% at 473 K, which could be further enhanced to 155  $g_{PO} kg_{cat}^{-1} h^{-1}$  at 493 K, still maintaining a high selectivity of 88% (GHSV = 10,000 mL  $g_{cat}^{-1} h^{-1}$ ). This performance is comparable to the best activities reported to date for catalysts without promoters.

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# Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jcat.2016.10.004.

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