Direct epoxidation of propene on silylated Au-Ti catalysts

Citation for published version (APA):

Kanungo, S., Keshri, K. S., Hensen, E. J. M., Chowdhury, B., Schouten, J. C., & Neira D'Angelo, M. F. (2018). Direct epoxidation of propene on silylated Au-Ti catalysts: A study on silylation procedures and the effect on propane formation. *Catalysis Science & Technology*, 8(12), 3052-3059. <https://doi.org/10.1039/C8CY00439K>

DOI:

[10.1039/C8CY00439K](https://doi.org/10.1039/C8CY00439K)

Document status and date:

Published: 01/05/2018

Document Version:

Accepted manuscript including changes made at the peer-review stage

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
- The final author version and the galley proof are versions of the publication after peer review.
- The final published version features the final layout of the paper including the volume, issue and page numbers.

[Link to publication](#)

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license above, please follow below link for the End User Agreement:

www.tue.nl/taverne

Take down policy

If you believe that this document breaches copyright please contact us at:

openaccess@tue.nl

providing details and we will investigate your claim.

Direct epoxidation of propene on silylated Au-Ti catalysts: A study on silylating procedures and effect on propane formation

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

S. Kanungo^a, K. S. Keshri^c, E. J. M. Hensen^b, B. Chowdhury^c, J. C. Schouten^a, M. F. Neira d'Angelo^{a*}

Silylation was employed on an active Au/Ti-SiO₂ catalyst, in order to enhance catalyst performance for the direct epoxidation of propene to propene oxide (PO) using H₂ and O₂. The effect of using different silylating agents and procedures on surface hydrophobicity and subsequently on catalytic activity was systematically investigated. The best performing catalysts were found to be those prepared by gas phase silylation after Au deposition, using hexamethyldisilazane (HMDS) and tetramethyldisilazane (TMDS) as silylating agents. The time of silylation was found to be critical for obtaining enhanced catalyst performance. An increase in PO yield, selectivity and H₂ efficiency was observed on silylation. Interestingly silylation also led to suppression of propene hydrogenation which is a major drawback of the process. The enhancement in catalytic performance is attributed to an increase in hydrophobicity and to blocking of unwanted Ti-OH sites that are potential sites for propane formation.

Introduction

Propene oxide (PO) is an important chemical intermediate which finds application in the production of polyether polyols, propene glycols and glycol ethers¹. The annual worldwide production capacity of PO reached 7.7 million tons in 2012 and is expected to grow up to 9.5 million tons in 2018². PO is currently produced by four different processes, i.e. the chlorohydrin, organic hydroperoxide, cumene recycling and hydrogen peroxide (HPPO) processes. Each process faces disadvantages such as multiple reaction steps (chlorohydrin, organic hydroperoxide, cumene recycling processes), production of hazardous by-products (chlorohydrin process) and the use of an expensive reactant (HPPO)^{1,3,4}. Accordingly, there is considerable scope for the development of a direct one-step oxidation process of propene to PO^{5,6}. In the presence of hydrogen and oxygen, propene can be directly epoxidized to PO over Au-Ti catalysts with very high selectivity with only water as the major side-product. Some of the factors that hamper its practical application are low propene conversion and H₂ efficiency^{3,7,8}.

The most active catalysts reported for this reaction are Au nanoparticles dispersed on Ti containing supports like TiO₂⁸, Ti-SiO₂⁹, Ti-MCM-41^{10,11}, Ti-SBA-15¹², TS-1^{13,14}. The active site for

epoxidation is proposed to be the Au-Ti interface, likely involving isolated-tetrahedral Ti sites in close proximity of Au particles with an optimal size of 2-5 nm. The widely accepted mechanism involves the formation of peroxy species (OOH*) on Au nanoparticles, which are spilled over to adjacent Ti sites forming Ti-OOH species, which react further with propene to yield PO and water^{15,16,17}. An active catalyst that has shown considerable potential in past studies is Au/Ti-SiO₂ where the support is synthesized by grafting Ti on the surface of silica⁹. A stable performance with the production of PO in the order of 100 g_{PO}.kg_{cat}⁻¹.h⁻¹ (200 °C, GHSV = 10000 mL.g_{cat}⁻¹.h⁻¹) was reported. This was achieved by lowering Au and Ti loadings, but alongwith high PO formation rates excessive propane formation was also observed⁹. The same authors also reported that the addition of CO to the feed can suppress propene hydrogenation¹⁸. Later it was found that the formation of propane can be controlled to some extent by optimizing the Ti grafting procedure^{19,20}. Other groups have also reported propane formation on different catalysts²¹⁻²⁴ along with other side-products (acetone, propanal, acrolein, acetaldehyde and CO₂) but the origin of propane formation remains under debate. While some studies suggest that the Au particle size is a determining factor²¹, the support itself may also have a role to play as shown by Chen et al^{25,26}. The formation of propane and an excessive amount of water (by direct hydrogen oxidation on isolated Au sites¹⁹) significantly lowers the hydrogen efficiency of the process. For this process to become commercially relevant, it is imperative to achieve higher hydrogen efficiencies (>50%) at high propene conversion (>10%) with r_{PO} > 100 g_{PO}.kg_{cat}⁻¹.h⁻¹³.

Silylation as a post-treatment procedure has proved to be useful for improving catalyst performance²⁷⁻³⁶. Silylation involves exposing the catalyst to a silylating agent which leads to the replacement of

^a Laboratory of Chemical Reactor Engineering, Department of Chemical Engineering and Chemistry Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

^b Laboratory of Inorganic Materials Chemistry, Schuit Institute of Catalysis, Department of Chemical Engineering and Chemistry Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

^c Department of Applied Chemistry, Indian Institute of Technology (Indian School of Mines), Dhanbad 826004, India

*Corresponding author: m.f.neira.dangelo@tue.nl

† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

surface hydroxyls with R_3Si groups. Typical agents include hexamethyldisilazane (HMDS)^{27,33,37}, trimethylchlorosilane (TMCS)^{29,38}, triethoxyfluorosilane (TEFS)³⁹, (trimethylsilyl)trifluoroacetamide (MSTFA)³⁵, methoxytrimethylsilane (TMMS)^{11,20,35} and tetramethyldisilazane (TMDS)³³. Silylation is generally accompanied by an increase in surface hydrophobicity which is proposed to be the underlying cause of the observed change in catalytic activity. Desorption of polar products is facilitated by the hydrophobic surface thereby arresting further reaction to form side products⁴⁰. But apart from hydrophobicity other factors may also be involved in enhancing catalyst activity as evidenced by our latest study where we found that the effect of silylation was highly dependent on the Au and Ti content²⁰. Furthermore the use of different silylating agents and procedures may alter the catalyst properties differently thus effecting the resulting catalytic performance. Hence a comprehensive study using different silylating approaches is required to further exploit the beneficial effects of silylation in an optimal manner.

Herein, we report the impact of silylating agents and procedures on the direct epoxidation of propene on Au/Ti-SiO₂ catalysts. Silylation was performed using TEFS, TMCS, TMDS and HMDS, either in the liquid and/or in the gas phase. We also investigated the influence of silylation before and after gold deposition. Significant improvement in catalyst performance was found when silylation was carried out in the gas phase on the Au loaded catalysts. Among the silylating agents studied, HMDS and TMDS showed the best improvement where a gain in PO yield, H₂ efficiency and suppression of propane formation was recorded post silylation. The time of silylation was found to be an important parameter that dictated post silylation activity. Our study shows the importance of choosing the suitable silylation technique in order to enhance catalyst performance. Moreover apart from facilitating product desorption owing to improved hydrophobicity, silylation was also found to effectively block unwanted sites for side reactions thereby inhibiting propane formation.

Experimental Methods

Catalyst synthesis

The silica support was modified using a known procedure²⁰. In a typical synthesis, as-received silica (15 g, Davisil-643, 300 m²/g, average pore size 150 Å, pore volume 1.15 cm³/g) was dried and suspended in 250 mL anhydrous 2-propanol (Aldrich, 99%) in a N₂-flushed glove-box. This suspension was stirred for 10 min after which tetraethylorthotitanate (TEOT, Aldrich, 97%) was added in such amount that the Ti coverage was 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% of the monolayer coverage. After stirring the slurry for 30 min, 2-propanol was slowly evaporated using a rotary evaporator at 55 °C and 100 mbar. Evaporation of the solvent took around 90 min. The powder obtained was dried overnight at 80 °C, followed by calcination at 120 °C (heating rate 5 °C/min, isothermal period 2 h) and 600 °C (heating rate 10 °C/min; isothermal period 4 h). As a reference, a titanosilicate (TS-1) zeolite

with a Si/Ti ratio of 100 was used prepared according to literature⁴¹. Gold was deposited on Ti-SiO₂ using a deposition-precipitation method described by Chen et al.²⁵. The support (1 g) was dispersed in 50 ml ultra-pure water (18.2 MΩ.cm at 25 °C). The pH was adjusted to ~9.5 using an aqueous 2.5 wt% ammonia solution. The desired amount of HAuCl₄ (Aldrich, 30 wt% in HCl) was diluted in 10 ml water, which was then added dropwise using a burette in ca. 15 min. Thereafter, the slurry was kept stirring for 1 h, while maintaining the pH at 9.4-9.5 by adding ammonia dropwise. The solid was collected by filtration, washed three times using 100 ml of deionized water. The catalyst was dried overnight at 80 °C and calcined at 120 °C (heating rate 5 °C/min, isothermal period 2 h) and 400 °C (heating rate 10 K/min, isothermal period 4 h) in static air. The catalysts are denoted as Au(x)/Ti(y)-SiO₂, where x is the nominal Au loading (in wt %) and y is the percentile monolayer coverage.

Silylation techniques

In this section, we describe the silylation procedures used for each silylating agent. The different approaches are summarized in Scheme 1 and the respective reactions can be found in the Supporting Information.

Triethoxyfluorosilane (TEFS): The treatment was performed following the method reported by Kosinov et al.³⁹. Prior to the treatment, 1 g of support was soaked in ethanol/water (2/1) solution overnight at room temperature. Then the powder was dried at 100 °C for 3 h. For the treatment, the support and 7 mL of 50 mM TEFS solution in acetonitrile were stirred for 5 h at room temperature. Afterwards, the solution was filtered, washed with acetonitrile and the powder dried overnight at 100 °C. For calcination, the powder was heated to 500 °C at a rate of 1 °C/min with an isothermal period of 8 h.

Trimethylchlorosilane (TMCS): Silylation with TMCS was done in the liquid and the gas phase. For the former, the substrate was treated by two different methods as reported by Tatsumi et al.²⁹ and Sun et al.³⁸. The first protocol was carried out at room temperature where 1 g of support, 2 mL of TMCS and 3 mL of 1,1,3,3-tetramethyldisiloxane (TMDSO) were refluxed overnight in N₂, under stirring. This was followed by filtration with acetone and drying at 120 °C for 3 h. The second protocol was carried out at 80 °C where 1 g of support, 75 mL of toluene and 5 mL of TMCS were refluxed for 8 h in N₂, under stirring. This was followed by filtration, washing twice with toluene and lastly with ethanol and finally drying overnight at 80 °C. For the gas phase silylation using TMCS, the method of Lin et al.³¹ was employed, with modifications. Vapors of TMCS were passed for 5 min through a bed of 0.3 g catalyst, which was maintained at 200 °C. Gaseous TMCS was obtained by bubbling He through a saturator containing TMCS, kept at 25 °C. The silylation step was followed by flushing with He at 200 °C for 5 h. Then, the catalyst was washed with methanol and DI water to remove Cl⁻ followed by drying at 80 °C for 1 h.

Hexamethyldisilazane (HMDS) and Tetramethyldisilazane (TMDS): Silylation procedure using HMDS and TMDS were adapted from Capel-Sanchez et al.³³ Vapors of the silylating agent were passed through a bed of 0.3 g catalyst, maintained at 200 °C, by bubbling He through a saturator containing the silylating agent, kept at 25 °C. The silylation step was followed by flushing with He at 200 °C for 2 h.

The resulting materials are denoted as Au/Ti-SiO₂-X-Y, where X represents the silylating agent, Y is G for gas phase silylation and L for liquid phase silylation. For those samples where Au deposition carried is out after silylation, the catalysts are denoted Ti-SiO₂-X-Y-Au.

Scheme-1: Summary of silylating procedure carried out using different silylating agents.

Catalyst characterization

The co-ordination environment of Ti was determined by diffuse reflectance UV-Vis (DR-UV-Vis) spectra using a Shimadzu UV-2401PC spectrometer with BaSO₄ as the reference.

The metal content was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) in a SpectroCiros CCD spectrometer. The metals were extracted in aqua regia under heating and 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 distribution of the Au particles. TEM images were recorded using a FEI Tecnai G2Sphera transmission electron microscope at an accelerating voltage of 200 kV. Sample preparation involved sonication of the finely ground catalyst in ethanol and application of a few drops of the suspension onto a TEM grid. The size distribution was determined by counting all visible gold particles from approximately 20 images using the ImageJ software.

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 (~8 µL) was placed on its surface using a needle. Images clearly showing the liquid-solid interface were collected and left and right contact angles were measured using the Dataphysics software. The average of these two measurements is reported as the contact angle. Thermogravimetric analysis (TGA) data profiles were measured using Mettler Toledo TGA/DSC.

The IR spectra was measured using Perkin Elmer Spectrum Two FTIR spectrophotometer. The samples were dried at 100 °C prior to characterization and were mixed with dry KBr to prepare pellets. The data was recorded at 30°C in the wave number range of 400-4000 cm⁻¹ with energy resolution of 4 cm⁻¹.

Catalytic activity measurements

Catalytic activity measurements were performed in a flow set-up 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 (ID = 4 mm) which was placed in a tubular oven. A typical reaction cycle was

5 h followed by a regeneration step at 300 °C with 10 vol % O₂ 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 = 10000 ml.g_{cat}⁻¹.h⁻¹). Reaction cycles were carried out typically in the temperature range 150-240 °C.

The propene conversion (X) and selectivity to different products (S_x where x denotes the product) were calculated considering the reaction $n\text{C}_3\text{H}_6 \rightarrow m\text{C}_x$ and expressed as:

$$X(\%) = \frac{\sum \frac{n}{m} P_x}{P_{\text{C}_3\text{H}_6}^{\text{out}} + \sum \frac{n}{m} P_x} \times 100 = \frac{\sum \frac{n}{m} P_x}{P_{\text{C}_3\text{H}_6}^{\text{in}}} \times 100 \quad (1)$$

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

where P_x is the partial pressure of the carbon-containing products obtained during the epoxidation of propene (PO, acrolein, acetone, propanal, acetaldehyde, propane and CO₂) and the terms $P_{\text{C}_3\text{H}_6}^{\text{in}}$ and $P_{\text{C}_3\text{H}_6}^{\text{out}}$ denote the propene concentrations at the inlet and outlet of the reactor respectively. H₂ efficiency is defined as:

$$\eta_{\text{H}_2}(\%) = \frac{r_{\text{PO}}}{r_{\text{PO}} + r_{\text{H}_2\text{O}} + r_{\text{C}_3\text{H}_8}} \times 100 \quad (3)$$

where r_{PO} , $r_{\text{H}_2\text{O}}$ and $r_{\text{C}_3\text{H}_8}$ are the rates of PO, water and propane respectively.

The rate, conversion, selectivity and H₂ efficiency for each catalytic cycle was calculated as the average of each quantity between 150 min to 300 min on stream.

The absence of mass transfer limitations was verified using the Weisz-Prater Criterion ($C_{\text{WP}} < 1$) and the Mears Criterion ($C_{\text{M}} < 0.15$) for internal and external mass transfer limitations, respectively. C_{WP} was found to be in the order of 10⁻⁶ (<< 1) and C_{M} in the order of 10⁻⁷ (<< 0.15), thus ensuring the system to be free of mass transfer limitations (Supporting Information).

Results and Discussion

Catalyst characterization

The diffuse reflectance UV-Vis (DR UV-Vis) spectra of different supports directly after calcination are shown in Fig. 1. The TS-1 (Si/Ti = 100) reference exhibits a main absorption band at 210 nm, indicating that most Ti atoms are tetrahedrally coordinated in the zeolite framework⁴². A high Ti dispersion and tetrahedral coordination is also observed for Ti(1)-SiO₂. A weak absorption feature of Ti(1)-SiO₂ at 250 nm can be assigned to Ti species in higher co-ordination⁴³. The support Ti(5)-SiO₂ exhibits a broader absorption range, up to 350 nm, indicative of larger fractions of penta and octa co-ordinated Ti, along with the presence of TiO_x agglomerates⁴³⁻⁴⁵.

Fig. 1: DR-UV-vis spectra of the three different supports having Ti monolayer coverage of 5% (red), 1% (blue) and TS-1(Si/Ti=100).

The two catalysts prepared on these supports were Au(0.1)/Ti(1)-SiO₂ and Au(1)/Ti(5)-SiO₂ with actual Ti loadings (percentile monolayer coverage between brackets) as 0.22 wt% (1 % ML) and 1.19 wt% (5 % ML) and Au loadings as 0.15 wt% and 0.88 wt% respectively, as revealed by elemental analysis. The respective average gold particle sizes determined by TEM are 1.7±0.8 nm and 3.1±1.4nm.

Effect of silylation on hydrophobicity

Silylation of supports followed by Au deposition

Fig. 2 shows the impact of silylation on Ti(1)-SiO₂. The contact angles are shown after the support is silylated using different agents. Contact angles were also measured after Au deposition on these silylated. The liquid-phase treatment with TMCS and TEFS slightly increased the hydrophobicity of Ti(1)-SiO₂. A more significant increase in the contact angle was observed when TMCS was used in combination with TMDSO. It was observed that the treated support was so hydrophobic that it was difficult to disperse in water, so Au deposition in aqueous suspension could not be carried out and ethanol was used as a dispersing medium. As shown in Fig. 2, the Au deposition procedure led to severe loss of hydrophobicity, as the contact angle was reduced to that of the untreated support *ca.* 7°. Decrease in hydrophobicity post Au deposition was also observed for supports silylated by TMCS and TEFS. This indicates that silylation followed by Au deposition by traditional deposition-precipitation method, is not a promising route as it may lead to loss of hydrophobicity. Moreover, it also leads to lower Au loadings than desired due to the unavailability of hydroxyls in the silylated support. This was evidenced by the support silylated with TEFS where ICP-OES revealed 0.08wt% Au content compared to 0.1wt% target loading. For this reason the gas phase silylation procedures were carried out only after Au deposition.

Fig. 2: (a) Contact angles obtained using different silylating agents (in solid colors) and after they are subjected to gold deposition (color with pattern), the support used is Ti(1)-SiO₂ (b) representative images showing contact angle measurement

Silylation of Au loaded catalysts

Silylation of Au(0.1)/Ti(1)-SiO₂ was conducted in the gas phase using TMCS, HMDS and TMDS. The contact angles of the silylated catalysts are shown in Fig. 3. TMCS treatment led to only a small increase in contact angle, while HMDS and TMDS showed significant increase in contact angle and hence hydrophobicity. We also observe the effect of the time of silylation on hydrophobicity. When the catalyst was silylated using HMDS for 10 min, the contact angle observed was 53° while the use of TMDS at same silylating time and conditions, led to a contact angle of 125°. This indicates that TMDS is a more efficient silylating agent. The presence of lower number of methyl groups in TMDS (four as opposed to six in HMDS), reduces steric hindrance during its reaction with hydroxyls³⁴. The importance of silylating time and its implication on catalytic activity will be discussed in the subsequent sections.

Fig. 3: (a) Contact angles obtained using different silylating agents and procedures on Au loaded catalyst, Au(0.1)-Ti(1)-SiO₂ (b) contact angles measured on unsilylated catalyst and after silylation by HMDS and TMDS

Effect of silylation on catalytic activity

From the observations so far, we infer that HMDS and TMDS were the most efficient in rendering hydrophobicity to our catalyst system. The respective catalytic activities for direct PO formation are shown in Fig. 4 and Table 1. In case of the unsilylated catalysts we observe from Fig. 4 that Au(0.1)/Ti(1)-SiO₂ is fairly active and very stable, with average rate of PO formation 80 g_{PO}/kg_{cat}/hr at 220 °C, in agreement

with past studies on similar catalysts^{18,25}. The PO formation is accompanied with significant amount of propane formation, also in agreement with literature¹⁸. The selectivities to PO and propane are 52% and 31%, respectively. The issue of propene hydrogenation in the direct epoxidation reaction is highly debatable. While earlier studies suggested that Au NPs < 2 nm were active sites for this reaction^{21,23}, recent studies on this catalyst have indicated the role of the support^{18,25}. It was observed that the Ti grafting time had a significant influence on deciding propane selectivity indicating that certain TiOx species or defect sites, were responsible for this side reaction^{20,25}. These catalysts prepared at different Ti grafting times exhibited a range of selectivities to propane (from 95% to 0%) and at the same time contained sub nanometer Au NPs as well, thus ruling out the possibility that Au particle size as the sole reason behind propane formation²⁰. Moreover, the observation of propane formation on the hydroxylated support (no Au) further confirmed the role of support and probably Ti-OH species in propene hydrogenation, in particular in case of supports where the Ti-O-Si and Ti-O-Ti groups are susceptible to hydrolysis²⁶.

Fig. 4: (a) Time-on-stream formation rate of PO and during a 5 h catalytic test over Au(0.1)/Ti(1)-SiO₂ that are unsilylated (triangle), silylated by HMDS (inverted triangle) and TMDS (circle) at H₂/O₂/C₃H₆/He = 1:1:1:7, GHSV = 10000 mL.g_{cat}⁻¹.h⁻¹.

Upon silylation with HMDS, the selectivity to propane goes down from 31% to 7% at the same reaction conditions. An increase of PO selectivity from 52% to 83% is observed, along with decrease in selectivity to CO₂ and other products. Interestingly, we see that propene conversion goes down from 5.9% in the unsilylated catalyst to 4.7% in the silylated one, indicating that propene hydrogenation occurs in parallel and on different sites compared to epoxidation. These sites are likely blocked upon silylation which leads to a drop in overall propene conversion. Chen et al²⁶ had reported complete suppression of propane formation by co-feeding small amounts of CO with the reaction mixture on a similar catalyst. These observations indicate a similar role of the silylating agent as CO, blocking the propene hydrogenation sites by forming -Ti-O-SiR₃ species. The resulting PO formation observed is stable with time on stream, as shown in Fig. 4 and the average rate of PO formation increases from 80 $g_{PO}/kg_{cat}/h$ to 101 $g_{PO}/kg_{cat}/h$. When the same silylation procedure was repeated with TMDS, it was observed that the resulting catalyst was hardly active and showed propene conversion <0.5% at same reaction conditions. An increase in reaction time and cycles with intermittent regeneration steps in O₂ at 300 °C, were also ineffective to increase activity, indicating that the active sites were completely blocked post the silylation procedure. Hence the silylation time was reduced to 5 min and the resulting activity is reported in Fig. 4 and Table 2. It can be observed that TMDS silylation led to a complete suppression of propane

formation, along with a drop in the rate of PO formation. A higher reaction temperature was required to get similar rates of PO as the unsilylated catalyst and even at this condition, PO selectivity was as high as 90%, with no observable propane formation.

To further verify the positive effect of the silylation procedure developed in this study, another catalyst, Au(1)/Ti(5)-SiO₂ was chosen, which had shown the maximum improvement in performance on silylation in a previous study²⁰. The activity results are shown in Table 1, where we see that on silylation with HMDS, the selectivity to PO increased from 86% to 90% and there was marked increment in the rate of PO produced, from 36 $g_{PO}/kg_{cat}/h$ to 60 $g_{PO}/kg_{cat}/h$. This shows the flexibility of this method to enhance activity of a different catalyst and also indicates that silylation had a more pronounced effect on activity of catalysts with higher Ti loading, which is in agreement with previous report²⁰. This observation further establishes the conversion of Ti sites (from Ti-OH to Ti-O-SiR₃) due to silylation. It must be noted here that no significant change in Au particle size (TEM measurements) and Au and Ti (ICP-OES) contents were observed before and after silylation in these catalysts. Hence the change in catalyst performance can be attributed to the silylation of the surface hydroxyl groups and not to the change in the number/nature of the active sites.

Effect of silylation time

Since silylation time was found to have a significant impact on the catalytic activity of the silylated catalyst, its effect was studied using TGA as shown in Fig. 5. We observe that the HMDS-10min and TMDS-5min have an identical weight loss profile, with significant weight loss beyond 550 °C, which is likely due to the decomposition of Si-O-Si (CH₃)₃ and Ti-O-Si (CH₃)₃. The TMDS-10min sample on the other hand, records significant overall weight loss. This clearly indicates that increasing the silylation time results in accumulation of unreacted TMDS on the catalyst surface that is lost at temperatures > 300 °C. This unreacted/excess amount of TMDS adsorb strongly on the catalyst surface, blocking the active sites. Flushing with He at 200°C after silylation, as followed in the silylation procedure, is not sufficient to remove these excess molecules. This step should, therefore be carried out at much higher temperatures ca. 300-500°C. But a higher flushing temperature may lead to sintering of the Au nanoparticles thus altering the catalyst, hence optimizing the silylation time seems to be a better alternative.

Fig. 5: TG profiles of unsilylated Au(0.1)/Ti(1)-SiO₂ (grey solid line) and after silylation using HMDS for 10 min (grey, dash dot), TMDS for 10 min (pink, dash) and TMDS for 5 min (pink solid line) from 50 °C to 750 °C

Table 1: Performance of silylated and unsilylated catalysts

Catalyst	Au and Ti loadings, wt%*	Reaction temperature (°C)	Conversion (%)	Selectivity (%)				H ₂ Efficiency, η_{H_2} (%)	r_{PO} (g _{PO} ·kg ⁻¹ ·cat·h ⁻¹)
				PO	C ₃ H ₈	CO ₂	Others		
Au(0.1)/Ti(1)-SiO ₂	0.15,	220	5.9	52	31	1.2	15.8	6	80
Au(0.1)/Ti(1)-SiO ₂ -HMDS	0.22	220	4.7	83	7	0	10	11	101
Au(0.1)/Ti(1)-SiO ₂ -TMDS		220	2.7	94	0	0	5	13.6	67
Au(0.1)/Ti(1)-SiO ₂ -TMDS		235	3.5	91	0	0	9	12.7	82
Au(1)/Ti(5)-SiO ₂	0.88,	150	1.5	86	0	0	14	7	35
Au(1)/Ti(5)-SiO ₂ -HMDS	1.19	150	2.6	90	0	0	10	12	60

*As found by ICP-OES

These catalysts were also studied using FTIR, as shown in Fig. 6. The band around 3450 cm⁻¹, representing the stretching mode of H-bonded silanols goes down substantially for both treatments, which is a direct evidence of silyl group incorporation by reaction with silanols³⁴. This is expectedly accompanied with the suppression of the peak at 1640 cm⁻¹, which arises from H-bonded silanol bending³⁴. In addition the peak at 960 cm⁻¹, assigned to Si-O-Ti bond or Si-OH groups^{11,34,47}, disappears. The peak at 2978 cm⁻¹ due to C-H oscillation³⁴ is not pronounced in TMDS-5min but becomes prominent when silylation is carried out for 10 min. Similarly, the peaks at 854 cm⁻¹, representing Si-C stretching vibration and that at 1260 cm⁻¹, due to Si-CH₃ bond stretching^{36,46,47} become more prominent on prolonging the silylation time. This indicates the presence of higher amounts of silylating agent on the 10 min silylated sample, in agreement with TGA data. Although the peaks due to the silylating treatment (due to silyl groups at 2978 cm⁻¹, 1260 cm⁻¹ and 854 cm⁻¹) become more pronounced on longer silylation, this is not accompanied by a decrease in the silanol group intensity (1640 cm⁻¹, 3450 cm⁻¹). This may indicate that on longer treatment, the silylating agent merely accumulates/adsorbs on the catalyst surface, without further reacting with the silanol groups. In other words, a silylation time of 5 min is sufficient to convert the silanols to Si-O-SiR₃ and further treatment leads to accumulation of the silylating agent, which in turn blocks the active sites for propene epoxidation, as observed from the catalytic results in the earlier section. The band around ~1100 cm⁻¹ is assigned to asymmetric Si-O-Si network vibrations with the corresponding symmetric vibration at 800 cm⁻¹, which are expectedly present in all the samples⁴⁸.

General Discussion

In this study we attempt to investigate the effect of different silylating techniques on Au-Ti catalysts for enhancing their activity towards the direct epoxidation of propene. It was found that silylating the supports prior to Au deposition rendered them hydrophobic (the extent depending on the silylation method followed). But upon Au deposition using conventional deposition precipitation method, the hydrophobicity effect was lost. This is likely due to the hydrolysis of Si-O-SiR₃ back to Si-OH during Au deposition, as it is carried out in aqueous medium. Solid grinding using an organic Au precursor as used by Haruta²¹, can be a potential alternative to overcome this problem. We also observed that carrying out silylation in the liquid phase, after Au deposition, led to

Fig. 6: IR Spectra of Au(0.1)/Ti(1)-SiO₂ unsilylated (grey solid line), silylated with TMDS for 5 min (pink solid line) and silylated with TMDS for 10 min (purple solid line).

extreme loss in catalytic activity, indicating blocking of the active sites by the silylating agent. Hence support silylation followed by Au deposition by conventional deposition-precipitation method and liquid phase silylation of the Au loaded catalyst, were concluded to be ineffective silylation techniques.

Gas phase silylation was carried out using HMDS, TMDS and TMCS. Silylation by HMDS and TMDS showed significant increase in contact angle, indicating successful hydrophobization. HMDS silylated catalyst showed an increase in PO selectivity and yield along with reduced propane formation. Silylation with TMDS was found to be faster than with HMDS and the silylation time was found to be critical for obtaining an optimally performing silylated catalyst. TGA measurements showed accumulation of excess silylating agent on increasing reaction time. IR measurements supported these findings and also showed conversion of hydroxyl groups, indicating successful silylation. TMDS silylated catalyst showed complete suppression of propane formation although a higher reaction temperature was required to attain same PO yield as the unsilylated one. The switching off of propane formation is proposed to be due to the conversion of defective Ti-OH sites to Ti-O-SiR₃, which further confirms the role of support in propene hydrogenation. Both the observations of faster

silylation time and total propane suppression as observed for TMDS, can be explained due to its smaller size (less steric hindrance) compared to HMDS. This makes TMDS an excellent choice for a

silylating agent, although further optimization of silylation time is required.

Conclusions

We have studied several silylation procedures to obtain an optimally performing silylated catalyst for the direct epoxidation of propene. Silylation after Au deposition and in the gas phase, were found to be the ideal combination. Gas phase silylation using HMDS and TMDS were found to greatly enhance the catalytic performance. While HMDS increased PO yield and selectivity, TMDS treatment led to a complete suppression of propane formation. Silylation of the catalyst with TMDS was much faster and silylation time was found to be a critical parameter for obtaining enhanced overall performance. The low propane formation observed on the silylated catalyst indicate the role of Ti species of the support which are likely blocked on silylation. Hence the enhancement in performance is a combined effect of increased hydrophobicity and blocking of unwanted reaction sites. These findings show the versatility of performing catalyst silylation for improving activity and the insights obtained can also be applied to other catalytic reactions.

Acknowledgements

The authors would like to acknowledge Netherlands Organization for Scientific Research (NWO) for financial support for this research, project number (10017587). We would also like to thank Fleur Marie Saint Germain for helping in the silylation experiments and dr. I. Jiménez Pardo for assisting in contact angle measurements. BC would like to acknowledge DST for funding in India-Netherland bi-lateral project (DST/INT/NL/FM/P-2/2013). KSK would like acknowledge Indian School of Mines for research fellowship.

References

- 1 H. Baer, M. Bergamo, A. Forlin, L. H. Pottenger and J. Lindner, *Ullmann's Encycl. Ind. Chem.*, 2012, 313–335.
- 2 D. M. Perez Ferrández, PhD thesis, Eindhoven University of technology, 2015.
- 3 J. Huang and M. Haruta, *Res. Chem. Intermed.*, 2012, 38, 1–24.
- 4 T. A. Nijhuis, M. Makkee, J. A. Moulijn and B. M. Weckhuysen, *Ind. Eng. Chem. Res.*, 2006, 45, 3447–3459.
- 5 S. J. Khatib and S. T. Oyama, *Catal. Rev. Sci. Eng.*, 2017, 57, 306–344.
- 6 J. R. Monnier, *Appl. Catal.*, 2001, 221, 73–91.
- 7 M. Haruta, *Chem. Rec.*, 2003, 3, 75–87.
- 8 T. Hayashi, K. Tanaka and M. Haruta, *J. Catal.*, 1998, 178, 566–575.
- 9 J. Chen, S. J. a Halin, E. A. Pidko, M. W. G. M. T. Verhoeven, D. M. P. Ferrandez, E. J. M. Hensen, J. C. Schouten and T. A. Nijhuis, *ChemCatChem*, 2013, 5, 467–478.
- 10 R. R. Sever, R. Alcala, J. A. Dumesic and T. W. Root, *Microporous Mesoporous Mater.*, 2003, 66, 53–67.
- 11 B. S. Uphade, T. Akita, T. Nakamura and M. Haruta, *J. Catal.*, 2002, 209, 331–340.
- 12 E. Sacaliuc, A. M. Beale, B. M. Weckhuysen and T. A. Nijhuis, *J. Catal.*, 2007, 248, 235–248.
- 13 X. Feng, N. Sheng, Y. Liu, X. Chen, D. Chen, C. Yang and X. Zhou, 2017, 7, 2668–2675.
- 14 W. S. Lee, M. Cem Akatay, E. A. Stach, F. H. Ribeiro and W. Nicholas Delgass, *J. Catal.*, 2012, 287, 178–189.
- 15 B. Chowdhury, N. Mimura, J. Lu, K. Bando and M. Haruta, *Phys. Chem. B*, 2006, 110, 22995–22999.
- 16 J. J. Bravo-Suárez, K. K. Bando, J. Lu, M. Haruta, T. Fujitani and S. T. Oyama, *J. Phys. Chem. C*, 2008, 112, 1115–1123.
- 17 S. Kanungo, Y. Su, M. F. N. Angelo, J. C. Schouten and E. J. M. Hensen, *Catal. Sci. Technol.*, 2017, 7, 2252–2261.
- 18 J. Chen, S. J. A. Halin, D. M. Perez Ferrandez, J. C. Schouten and T. A. Nijhuis, *J. Catal.*, 2012, 285, 324–327.
- 19 S. Kanungo, D. M. Perez Ferrandez, F. Neira d'Angelo, J. C. Schouten and T. A. Nijhuis, *J. Catal.*, 2016, 338, 284–294.
- 20 S. Kanungo, K. S. Keshri, A. J. F. van Hoof, M. F. N. d'Angelo, J. C. Schouten, T. A. Nijhuis, E. J. M. Hensen and B. Chowdhury, *J. Catal.*, 2016, 344, 434–444.
- 21 C. Qi, J. Huang, S. Bao, H. Su, T. Akita and M. Haruta, *J. Catal.*, 2011, 281, 12–20.
- 22 S. Naito and M. Tanimoto, *Chem. Commun.*, 1988, 832–833.
- 23 T. Hayashi, K. Tanaka and M. Haruta, *J. Catal.*, 1998, 178, 566–575.
- 24 J. Gaudet, K. K. Bando, Z. Song, T. Fujitani, W. Zhang, D. Sheng and S. T. Oyama, *J. Catal.*, 2011, 280, 40–49.
- 25 J. Chen, S.J.A. Halin, E.A. Pidko, M.W.G.M.T. Verhoeven, D.M.P. Ferrandez, E.J.M. Hensen, J.C. Schouten and T.A. Nijhuis, *ChemCatChem*, 2013, 5, 467–478.
- 26 J. Chen, S.J.A. Halin, J.C. Schouten and T.A. Nijhuis, *Faraday Discuss.*, 2011, 152, 321–336
- 27 A. R. Almeida, J. T. Carneiro, J. A. Moulijn and G. Mul, *J. Catal.*, 2010, 273, 116–124.
- 28 M. R. Prasad, M. S. Hamdy, G. Mul, E. Bouwman and E. Drent, *J. Catal.*, 2008, 260, 288–294.
- 29 T. Tatsumi, K. A. Kyono and N. Igarashi, *Chem. Commun.*, 1998, 325–326.
- 30 S. Lee, Y. Lee, J. Kim and S. Jeong, *Appl. Catal. B Environ.*, 2017, 219, 1–9.
- 31 K. Lin, L. Wang, F. Meng, Z. Sun, Q. Yang, Y. Cui, D. Jiang and F. S. Xiao, *J. Catal.*, 2005, 235, 423–427.
- 32 M. Ramakrishna Prasad, M. S. Hamdy, G. Mul, E. Bouwman and E. Drent, *J. Catal.*, 2008, 260, 288–294.

- 33 M. C. Capel-Sanchez, J. M. Campos-Martin and J. L. G. Fierro, *Catal. Today*, 2010, 158, 103–108.
- 34 C. Qi, T. Akita, M. Okumura, K. Kuraoka and M. Haruta, *Appl. Catal. A Gen.*, 2003, 253, 75–89.
- 35 B. Chowdhury, K. K. Bando, J. J. Bravo-Suarez, S. Tsubota and M. Haruta, *J. Mol. Catal. A Chem.*, 2012, 359, 21–27.
- 36 M. V. Cagnoli, S. G. Casuscelli, A. M. Alvarez, J. F. Bengoa, N. G. Gallegos, M. E. Crivello, E. R. Herrero and S. G. Marchetti, *Catal. Today*, 2005, 107–108, 397–403.
- 37 (a) M. Weisbeck, C. Schild, G. Wegener, G. Wiesmeier, DE19918431, 2000 (to Bayer).; (b) M. Weisbeck, G. Wegener, G. Wiesmeier, P. Vogtel, WO2011041921, 2001 (to Bayer).
- 38 J. Sun, D. Ma, H. Zhang, X. Liu, X. Han, X. Bao, G. Weinberg, N. Pfander and D. Su, *J. Am. Chem. Soc.*, 2006, 128, 15756–15764.
- 39 N. Kosinov, V. G. P. Sripathi and E. J. M. Hensen, *Microporous Mesoporous Mater.*, 2014, 194, 24–30.
- 40 M. L. Pea, V. Dellarocca, F. Rey, a. Corma, S. Coluccia and L. Marchese, *Microporous Mesoporous Mater.*, 2001, 44–45, 345–356.
- 41 L. Y. Chen, G. K. Chuah and S. Jaenicke, *J. Mol. Catal. A Chem.*, 1998, 132, 281–292.
- 42 G. N. Vayssilov, *Catal. Rev.*, 1997, 39, 209–251.
- 43 J. M. Fraile, J. I. García, J. a. Mayoral and E. Vispe, *J. Catal.*, 2005, 233, 90–99.
- 44 X. Gao and I. E. Wachs, *Catal. Today*, 1999, 51, 233–254.
- 45 O. A. Kholdeeva, I. D. Ivanchikova, M. Guidotti, C. Pirovano, N. Ravasio, M. V. Barmatova and Y. A. Chesalov, *Adv. Synth. Catal.*, 2009, 351, 1877–1889.
- 46 J. Bu and H. Rhee, *Catal. Lett.*, 2000, 66, 245–249.
- 47 J. Bu and H. Rhee, *Catal. Lett.*, 2010, 65, 141–145.
- 48 R.S. Drago, S.C. Dias, J.M. McGilvray and A.L.M.L. Mateus, *J. Phys. Chem. B*, 1998, 102, 1508–1514.