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ARTICLE

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

S. Kanungo, K. S. Keshri, E. J. M. Hensen, B. Chowdhury, J. C. Schouten, M. F. Neira d’Angelo*

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 ethers. 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 2018. 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). Accordingly, there is considerable scope for the development of a direct one-step oxidation process of propene to PO. 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.

The most active catalysts reported for this reaction are Au nanoparticles dispersed on Ti containing supports like TiO₂, Ti-SiO₂, Ti-MCM-41, Ti-SBA-15, TS-1. 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. 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 silica. A stable performance with the production of PO in the order of 100 gPO kg⁻¹ cat⁻¹ h⁻¹ (200 °C, GHSV = 10000 mL g⁻¹ cat⁻¹ h⁻¹) was reported. This was achieved by lowering Au and Ti loadings, but along with high PO formation rates excessive propane formation was also observed. The same authors also reported that the addition of CO to the feed can suppress propene hydrogenation. Later it was found that the formation of propane can be controlled to some extent by optimizing the Ti grafting procedure. Other groups have also reported propane formation on different catalysts along with other side-products (aceton, 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 factor, the support itself may also have a role to play as shown by Chen et al. The formation of propene and an excessive amount of water (by direct hydrogen oxidation on isolated Au sites) 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 rPO > 100 gPO kg⁻¹ cat⁻¹ h⁻¹.

Silylation as a post-treatment procedure has proved to be useful for improving catalyst performance. Silylation involves exposing the catalyst to a silylating agent which leads to the replacement of the oxide surface with silyl groups on the surface of the catalyst. This modifies the surface hydrophobicity thereby reducing the rate of hydrogenation of propene. The silylation process is also believed to enhance the dispersion of the Au particles on the support and thereby enhance the catalytic activity.

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surface hydroxyls with $R_3Si$ groups. Typical agents include hexamethyldisilazane (HMDS)\textsuperscript{27,33,37}, trimethylchlorosilane (TMCS)\textsuperscript{29,38}, triethoxyfluorosilane (TEFS)\textsuperscript{19}, (trimethylsilyl)trifluoroacetamide (MSTFA)\textsuperscript{35}, methoxytrimethylsilane (TMMS)\textsuperscript{31,20,35} and tetramethyldisilazane (TMDS)\textsuperscript{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 products\textsuperscript{40}.

Typical synthesis, as-received silica (15 g, Davisil-643, 300 m$^2$/g, average pore size 150 Å, pore volume 1.15 cm$^3$/g) was dried and suspended in 250 mL anhydrous 2-propanol (Aldrich, 99%) in a N\textsubscript{2}-flushed glove-box. This suspension was stirred for 10 min after which the solution was filtered, 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 10 K/min, isothermal period 4 h) in static air. The catalysts are denoted as Au(x)/Ti(y)-SiO$_2$, 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.\textsuperscript{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 was 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.\textsuperscript{29} and Sun et al.\textsuperscript{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 N$_2$ 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 N$_2$, 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.\textsuperscript{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.\textsuperscript{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.

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**Experimental Methods**

**Catalyst synthesis**

The silica support was modified using a known procedure\textsuperscript{20}. In a typical synthesis, as-received silica (15 g, Davisil-643, 300 m$^2$/g, average pore size 150 Å, pore volume 1.15 cm$^3$/g) was dried and suspended in 250 mL anhydrous 2-propanol (Aldrich, 99%) in a N$_2$-flushed glove-box. This suspension was stirred for 10 min after which the solution was filtered 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.

The catalyst 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 literature\textsuperscript{41}. Gold was deposited on Ti-SiO$_2$ using a deposition-precipitation method described by Chen et al.\textsuperscript{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 HAuCl$_4$ (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 10 K/min, isothermal period 4 h) in static air. The catalysts are denoted as Au(x)/Ti(y)-SiO$_2$, where x is the nominal Au loading (in wt %) and y is the percentile monolayer coverage.

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**Please do not adjust margins**
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.

![Catalytic activity measurements](image)

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 swirled until clear. Dilute HF (1:15 by volume in water) was added and the solution was heating and stirring for 30 min. The solutions were cooled and then the size distribution of the Au particles. TEM images were recorded using the ImageJ software.

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 absorption band at 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.gcat⁻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 (Sx, where x denotes the product) were calculated considering the reaction

\[
\begin{align*}
X(\%) &= \frac{\sum n_{P_x} P_{P_x}}{P_{C_3H_6}} \times 100 \\
S_x(\%) &= \frac{n_{P_x}}{n_{C_3H_6}} \times 100
\end{align*}
\]

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 \( P_x \) denote the propene concentrations at the inlet and outlet of the reactor respectively. H₂ efficiency is defined as:

\[
\eta_{H_2}(\%) = \frac{r_{H_2}}{r_{PO} + r_{H_2O} + r_{C_3H_8}} \times 100
\]

where \( r_{PO} \), \( r_{H_2O} \) and \( r_{C_3H_8} \) 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 Weiss-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 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 framework. 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 TiO₅ agglomerates43-45.
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.

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 gPO/kgcat/hr at 220 °C, in agreement...
with past studies on similar catalysts. The PO formation is accompanied with significant amount of propane formation, also in agreement with literature. The selectivities to PO and propane are 52% and 31%, respectively. The issue of propane formation in the direct epoxidation reaction is highly debatable. While earlier studies suggested that Au NPs < 2 nm were active sites for this reaction, recent studies on this catalyst have indicated the role of the support. 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. 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 formation. Moreover, the observation of propane formation on the hydroxylated support (no Au) further confirmed the role of support and probably Ti-OH species in propane hydrogenation, in particular in case of supports where the Ti-O-Si and Ti-O-Ti groups are susceptible to hydrolysis.

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)₂ and Ti-O-Si (CH₃)₂. 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.
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 silanols. In addition the peak at 960 cm⁻¹, assigned to Si-O-Ti bond or Si-OH groups, disappears. The peak at 2978 cm⁻¹ due to C-H oscillation 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 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 presence of higher amounts of silylating agent on the 10 min silylated catalysts were 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 the catalyst 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 is all the samples.

**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 propane. It was found that silylation 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 Haruta, 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 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 defective Ti-OH sites to Ti-O-SiR₃, which further confirms the role of support in propane hydrogenation. Both the observations of faster

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**Table 1: Performance of silylated and unsilylated catalysts**

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Au and Ti loadings, wt%</th>
<th>Reaction temperature (°C)</th>
<th>Conversion (%)</th>
<th>Selectivity (%)</th>
<th>H₂ Efficiency, ( \eta_{H₂} ) (%)</th>
<th>( r_{PO} ) (g PO kg⁻¹cat.h⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au(0.1)/Ti(1)-SiO₂</td>
<td>0.15, 0.22</td>
<td>220</td>
<td>5.9</td>
<td>52</td>
<td>31</td>
<td>1.2</td>
</tr>
<tr>
<td>Au(0.1)/Ti(1)-SiO₂-HMDS</td>
<td></td>
<td>220</td>
<td>4.7</td>
<td>83</td>
<td>7</td>
<td>0</td>
</tr>
<tr>
<td>Au(0.1)/Ti(1)-SiO₂-TMDS</td>
<td></td>
<td>220</td>
<td>2.7</td>
<td>94</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Au(0.1)/Ti(1)-SiO₂-TMCS</td>
<td></td>
<td>235</td>
<td>3.5</td>
<td>91</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Au(1)/Ti(5)-SiO₂</td>
<td>0.88, 1.19</td>
<td>150</td>
<td>1.5</td>
<td>86</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Au(1)/Ti(5)-SiO₂-HMDS</td>
<td></td>
<td>150</td>
<td>2.6</td>
<td>90</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

*As found by ICP-OES*
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 cataly st 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.

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