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Probing the gold active sites in Au/TS-1 for gas-phase epoxidation of propylene in the presence of hydrogen and oxygen

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ABSTRACT
Nanoporous gold particles supported on titania silicalite-1 catalysts (Au/TS-1) have shown high propylene oxide (PO) rate (~160 gPO h⁻¹ kg⁻¹) at ~200 °C and 1 atm for gas-phase epoxidation of propylene in the presence of hydrogen and oxygen. In this work, we address the issue of whether gold clusters inside TS-1 can be the active sites for the PO reaction. Coating TS-1 seeds with silicalite-1 produced a material (S-1/TS-1), which possessed a well-defined MFI structure, as shown by XRD and selected area electron diffraction, and Ti on the external surface could not be detected by XPS after addition of gold by deposition precipitation. The Au/S-1/TS-1 catalyst had at least 20 times higher PO rate (per gram of catalyst) at ~200 °C compared to that of a Au/TS-1 sample with similar gold loading at ~0.05 wt%. Since neither Au nor Ti alone gives any significant PO activity, this is the first direct experimental evidence showing that gold clusters inside the TS-1 are active for the PO reaction at H₂/C₃H₆/O₂/N₂ = 3.5/3.5/3.5/24.5 mL min⁻¹ and a space velocity of 14,000 mL h⁻¹ kg⁻¹. Furthermore, a much higher PO rate per gram of TS-1 for the Au/S-1/TS-1 catalyst (~240 gPO h⁻¹ kg⁻¹) than expected for a Au/TS-1 with similar gold loading at ~0.05 wt% and Si/Ti molar ratio from 65 to 100 (~60–140 gPO h⁻¹ kg⁻¹) implies that Au clusters inside the TS-1 nanoporous channels can be the dominant active sites for the PO reaction.

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1. Introduction

As discovered by Haruta and coworkers, propylene oxide (PO) can be produced catalytically by titania-supported gold catalysts (Au/TiO₂) when H₂ is co-fed together with propylene and O₂ [1,2]. The high PO selectivity (>99%) and the fact that water is the main byproduct make this reaction very attractive as a potential green hydrogen peroxide species from O₂ and H₂ over small gold clusters was also found to be energetically favorable from DFT calculations [11–13]. This supports the idea that small gold clusters inside the TS-1 nanopores can be active sites for the PO reaction, since it has been generally accepted that Au sites are responsible for the H₂O₂ generation and Ti sites for the epoxidation in the Au–Ti catalyst system [14,15]. On the other hand, Haruta and coworkers recently proposed that the gold clusters between 1 and 2 nm, prepared by a solid grinding (SG) method and too large to fit in the TS-1 nanopores, are the dominant active sites in Au/TS-1 for the PO reaction [4]. However, whether or not the gold clusters inside the TS-1 nanopores are active for the PO reaction remains unanswered. Recently, Xu and coworkers [16] synthesized MCM-41 type mesoporous silica-coated TS-1 material (mesoSiO₂ shell/TS-1 core), deposited gold on it, and ran the PO reaction at 10/10/10 bal vol% of C₃H₆/H₂/O₂/N₂ with a space velocity of 4000 mL h⁻¹ kg⁻¹ at 150 °C. Since neither Au nor Ti alone would give any significant PO activity [2,17,18], any apparent PO rate should come from the proximity between Au and Ti. Because a significant PO rate was observed on their Au/mesoSiO₂/TS-1, the authors proposed that gold particles confined in the coated mesoporous silica matrix (~2.5 nm pore diameter) could catalyze H₂ and O₂ to produce H₂O₂ in situ and that H₂O₂ could then diffuse into the TS-1 core...
for the epoxidation step to occur. However, whether the H₂O₂ can survive during the diffusion at the high reaction temperature (150 °C) remains unclear, since it is well known that H₂O₂ is not stable at high temperature. Furthermore, the authors could not exclude the possibility that the PO rate could come from the gold particles (<2.5 nm, confined in the coated mesoporous silica matrix) in proximity to the Ti sites on the external surface of the TS-1 core. Such proximate sites would not require long H₂O₂ lifetimes. On the other hand, these experimental results also imply that the gold clusters inside the nanocrystals of the TS-1 could be active for the PO reaction because the gold species were deposited by the deposition precipitation (DP) method, which would not exclusively occur in the mesoporous silica matrix only. Therefore, the PO activity assignment to the larger gold particles (outside the TS-1 nanocrystals) and/or the smaller gold clusters (inside the TS-1 nanocrystals) still remains unsolved. We have tackled this question via synthesizing a specially designed silicalite-1 (S-1)-coated titanium silicalite-1 (TS-1) material (i.e., a continuous crystal structure (MFI) in which no Ti is available on the external surface of the S-1/TS-1) as the support and then depositing gold on it to probe the activity of the small gold clusters inside the TS-1 nanocrystals. Since there is no possibility of making Au proximate to Ti on the external surface of S-1/TS-1 (because TS-1 is coated by S-1), the observed PO rate provides useful insight on the identification of the activity of the small gold clusters inside the TS-1 nanocrystals. No or little PO rate should be observed from this Au/S-1/TS-1 catalyst if (1) gold cannot get into the TS-1 (due to lack of the Au–Ti proximity) or (2) the gold clusters inside the TS-1 nanocrystals are not active for the PO reaction. The significant PO rate observed from the Au/S-1/TS-1 is attributed to the proximity between the Au and Ti in the TS-1 and thus directly proves that the small gold clusters inside the TS-1 nanocrystals are active for the PO reaction.

2. Experimental methods

2.1. S-1/TS-1 synthesis

TS-1 seeds were prepared following a method similar to that used in our previous paper [5,19], and the procedure for coating S-1 on the TS-1 seeds was adapted from Li et al. [20]. For the seed preparation, successive centrifugation was used to remove large crystallites. The TS-1 growth liquid, after the crystallization at 140 °C for about 20 h, was separated via centrifugation at 4500 rpm for 30 min (Eppendorf Centrifuge 5804). The separated solid (TS-1) was discarded, while the decanted TS-1 sol was then separated via centrifugation again (4500 rpm for 20 min). After centrifugation, the separated TS-1 solid was abandoned again while the decanted TS-1 sol suspension was kept. This decanted TS-1 sol was further separated via a high-speed centrifuge at 12,000 rpm for 15 min (Beckman Coulter Allegra 21 Centrifuge). The resulting solid, designed as the TS-1 seed, was washed by suspension in 100 mL deionized water (Millipore, Synergy UV Water Purification System, 18.2 MΩ cm²⁻¹ resistivity, hereafter denoted as D.I. water) and separated again by the high-speed centrifugation. This washing step was repeated one more time and the TS-1 seed (in the centrifuge tube, without a cap) was dried in the hood for few hours to remove excess water. About 2.3 g TS-1 seed sol (TS-1 seed + the remaining moisture) was then suspended in 200 mL of 0.1 M HCl solution with stirring rate 1150 rpm at 50 °C for ~44 h. The acid treatment was used to leach out any extramolecular Ti and/or reduce surface Ti content, which might potentially inhibit the growth of S-1 layers on the TS-1 seed [20]. After the acid treatment, the TS-1 seed was separated and washed by a total of 540 mL of D.I. water in a fashion similar to that described above. After this washing step, the TS-1 seed was then suspended in 125 mL of 0.1 M NH₄OH for 1 h at room temperature. The base-treated TS-1 seed was then separated via high-speed centrifugation, and most of the NH₄OH solution was decanted such that the seed content was about 25 wt%. The resulting TS-1 seed sol (TS-1 seed + NH₄OH solution) was about 8 g (no further drying) and was ready for the first S-1 coating.

The S-1 growth solution for the first S-1 coating was prepared by adding 12.8 mL of tetraethyloxysilicate (TEOS, Sigma, 98%) into 66.3 mL D.I. water, followed by drop-wise addition of 1.54 mL of tetrapropylammonium hydroxide (TPAOH, Alfa Aesar, 40 wt%) and 11.3 mL ethanol (EtOH, 200 proof). The S-1 solution was stirred for a few minutes and then the base-treated TS-1 seed sol (~8 g) was added. The final solution was further stirred at 60 °C for 1 h before being placed (with a stir bar inside) in a Teflon autoclave (Quetron Technologies) and then crystallized in a static oven (Precision Scientific) at 100–110 °C for 20 h under autogeneous pressure. We note that the Teflon liner was cleaned by filling it with a 50/50 mixture (by volume) of hydrofluoric acid (HF, Mallinckrodt 48%) and aqua regia (3:1 ratio of concentrated HCl/ HNO₃, Mallinckrodt) and aged for 1 day at room temperature to dissolve any residual Ti from previous TS-1 synthesis. During the 20 h period of crystallization, the autoclave vessel was occasionally taken out of the oven and put on a stir plate to promote the mixing of the solution by setting the stir rate ~500 rpm for about 5 min each time. After crystallization, the S-1/TS-1 crystallites were extracted via centrifugation at 4500 rpm for 9 min, instead of 30 min, in order to select the larger particles, which resulted from the S-1 coating. The size of the separated solid (S-1/TS-1) was then further screened via centrifugation for another two times. Each time, the sample was suspended in 50 mL D.I. water, centrifuged at 4500 rpm for 5 min, and the decanted solution containing the unseparated particles was discarded. The separated S-1/TS-1 was then suspended into 50 mL of 0.27 M NH₄OH solution and stirred at 900 rpm at room temperature overnight. The base-treated S-1/TS-1 was then separated and washed by 50 mL D.I. water via centrifugation (4500 rpm for 5 min). The separated S-1/TS-1 sol (S-1/TS-1 + water, a total of ~5.4 g) was suspended in 15 mL of 0.12 M NH₄OH solution for the second S-1 coating.

The S-1 growth solution for the second S-1 coating was prepared by adding 8.5 mL of TEOS into 44.2 mL D.I. water, followed by adding 1.02 mL TPAOH, 7.52 mL of ethanol and 1 mL of ethanolamine (Sigma, 99+% ACS reagent). The S-1 solution was then stirred for a few minutes, and then, the base-treated S-1/TS-1 sol (~20 g) was added. The final solution was further stirred at room temperature for 30 min before being placed in a Teflon autoclave (with a stir bar inside) and then crystallized at 100 °C for 8 h under autogeneous pressure. The promotion of the solution mixing during the 8 h was performed in a similar fashion as described above. After crystallization, the resulting second coated S-1/TS-1 was first separated via centrifugation and then washed twice with 50 mL D.I. water (4500 rpm for 5 min). This twice-coated product, hereafter denoted as S-1/TS-1 for simplicity, was dried in a vacuum oven at room temperature overnight and then calcined in a ceramic combustion boat (CoorsTek) in a Lindberg Blue M Tube Furnace at 550 °C for 16 h with a ramping rate ~2 °C min⁻¹ from RT in a flow of air ~200–300 mL min⁻¹ to remove the organic template.

2.2. Gold deposition

Gold was deposited using a modified deposition precipitation (DP) method. Approximately, 0.2 g (0.3 g for the repeat sample) of HAuCl₄·3H₂O (Alfa Aesar, 99.99%) was dissolved in ~40 mL of D.I. water and a specific amount of 1 N sodium carbonate with Na/ Au molar ratio ~5 (J.T. Barker Chemical Co.) was added to target the final pH of the gold slurry solution (the support + the gold
solution) to ~7–7.5. The neutralized gold solution was further stirred at a rate of 900 rpm for 5 h at room temperature. Meanwhile, approximately 0.6 g (1.8 g for the repeat sample) of S-1/TS-1 was dried in an oven (Precision Scientific) at 140 °C for at least 3 h before being added into the neutralized gold solution. The pH of the gold solution after neutralization and aging for 5 h was about 8, and the gold solution was nearly colorless, indicating that most of the chloride ligands were replaced by the hydroxyl ligands [21]. Then, the gold slurry solution was allowed to stir for another 4.5–5 h at room temperature, and the final pH of the gold slurry solution was about 7–7.5 (Mettler Toledo Seven Easy pH meter with pH electrodes: InLab®RoutinePro). The solid was then separated from the gold slurry solution via centrifugation (4500 rpm for 30 min), washed by suspension in approximately 50 mL D.I. water, and stirred for 1–2 min. The solid was separated via centrifugation again and dried in the vacuum oven at room temperature overnight. For Au/S-1 with different loadings from 0.019 wt% to ~0.05 wt%, the catalysts were prepared by either a similar fashion to that described above or the preparation method reported previously in [5], where the gold concentration was around 6.5–10 gAu/C144 3H2O L−1. The pH of the slurry was controlled at ~7.6–7.85, the mixing time was 5–9.5 h, and the preparation temperature was RT. In order to eliminate any Ti contamination inherent from the Teflon liners, which were previously used for TS-1 synthesis, ~10 g calcined S-1 was further suspended in 200 mL of 5 M nitric acid solution at 50 °C for 10 h. Following the acid pretreatment, the support was separated via centrifugation, washed by ~1 L D.I. water, which gave the pH of the decanted solution ~7, and dried in the static oven at 140 °C at least 3 h prior for gold deposition. This acid pretreated S-1 support was named as S-1(ap). Catalysts are named by gold loading and Si/Ti molar ratio (if applicable) such that a catalyst, 0.1Au/TS-1(100), represents that the gold loading is 0.1 wt% and the Si/Ti molar ratio is 100.

2.3. Characterization of gold on coated titanium silicalite-1

The coated material (S-1/TS-1) was characterized via TEM, XRD, XPS, DRUV-vis and N2 adsorption analysis at 77 K to understand the result of the S-1 coating and the corresponding influence on the spatial distribution of the titanium. The particle sizes as well as the crystal morphologies of both the TS-1 seed and the S-1/TS-1 materials were characterized via scanning electron microscopy (SEM, Hitachi, SU-70) and transmission electron microscopy (TEM, JEOL 2100 FEG, 200 keV). Gold particle sizes were determined by high resolution transmission electron microscopy (HRTEM, FEI Titan, 300 keV). The bulk structure of the S-1, S-1/TS-1 and the TS-1 seed were determined using X-ray diffraction (XRD, Scintag X2 diffractometer, CuKα with scanning rate 1.2° min−1) and selected area electron diffraction (SAED) patterns (TEM, JEOL 2100 FEG, 200 keV). The surface areas as well as the pore volumes were measured using N2 adsorption isotherms (Micromeritics ASAP 2000). Samples were degassed at 250 °C for at least 8 h before N2 analysis. The coordination of the titanium in the TS-1 seed was evaluated using diffuse reflectance ultraviolet–visible spectroscopy (DRUV-vis, Varian Cary 5000 outfitted with Harrick Praying Mantis optics and BaSO4 as the reference). The bulk gold and titanium contents were determined by atomic absorption spectroscopy (AAS, Perkin–Elmer AAAnalyst 300) and in some cases by energy dispersive spectroscopy (EDS) in a transmission electron microscope. The surface Ti content was obtained by X-ray photoelectron spectroscopy (XPS with a Kratos Axis Ultra DLD spectrometer using AlKα monochromatic X-ray radiation, 1486.6 eV), and the binding energy (BE) scale was referenced to the Si 2p line at 103.4 eV [22].

2.4. Measurement of PO reaction rate

The gas-phase epoxidation of propylene was carried out in a plug flow Pyrex reactor with 10 mm inner diameter. The reaction temperature was monitored by inserting a type K thermocouple into the catalyst bed, which typically consisted of ~0.15 g (sieved, 80–120 mesh size) catalyst and ~1–2 g quartz sand, 70–80 mesh, to improve the temperature uniformity within the catalyst bed. For some of the apparent activation energy measurements in the selected Au/S-1 samples, ~0.17–0.22 g catalyst was loaded to give a better signal for data analysis. A blank experiment confirmed that no PO rate was generated from the quartz sand or the blank reactor. A total flow rate of 35 mL min−1, consisting of 10/10/10/70 vol% of H2 (Praxair, 99.999%), O2 (Praxair, 99.999%), propylene (Matheson, 99.9%) and N2 (Matheson, 99.999%), was passed through the catalyst bed, resulting in a space velocity of 14,000 mL h−1 gcat. Typical pressure drop caused by the catalyst bed was ~0.5 psi. The reaction temperature, 200 ± 2 °C, was chosen to test the catalytic activity. The catalyst was heated in the reaction mixture from room temperature to 200 °C at a ramp rate of 0.5 or 1 °C min−1. The absence of external mass transfer was checked by calculating the Mears’ criterion (order of 10−7 < 0.15, Table S1 in the SI). Furthermore, the PO reaction was under differential conditions such that the conversions for propylene and H2 were less than 1% and 10%, respectively (Figs. S1 and S2 in the SI). Internal mass transfer limitations can be neglected because the estimated Thiele modulus is in the range of 10−1–10−2 (Table S2 in the SI). The effect of decay on the shelf was minimized by testing the catalyst within 24 h of gold deposition. The reactor effluent was analyzed using an Agilent 6890 gas chromatograph outfitted with an automatic sampling valve and two sample loops. Organic products (propylene, PO, ethanol (Et), propenal (Pr), acetonitrile (AcN), and acrolein (An)) were separated using a Supelcowax 10 capillary column (0.53 mm × 60 m) and analyzed via a flame ionization detector, while inorganic products (H2, O2 and CO2) were separated by a Chromosorb 102 packed column (1/8 in. × 8 ft) and analyzed by a thermal conductivity detector. The propylene conversion, PO selectivity, and H2 selectivity were calculated directly and defined as follows:

\[
\text{Propylene conversion} = \frac{\text{moles of (C}_1 - \text{oxygenates}}{\text{moles of propylene in the feed}}
\]

\[
+ \frac{\text{2/3 × ethanol}}{\text{moles of propylene in the feed}}
\]

\[
+ \frac{\text{CO}_2/3}{\text{moles of propylene in the feed}}
\]

\[
\text{PO selectivity} = \frac{\text{moles of PO/moles of (C}_1 - \text{oxygenates}}{\text{moles of propylene in the feed}}
\]

\[
+ \frac{\text{2/3 × ethanol}}{\text{moles of propylene in the feed}} + \frac{\text{CO}_2/3}{\text{moles of propylene in the feed}}
\]

\[
\text{H}_2\text{selectivity} = \frac{\text{moles of PO/moles of H}_2 \text{ converted}}{\text{moles of PO/moles of H}_2 \text{ converted}}
\]

However, use of nitrogen as the carrier gas prevented a precise quantification of the trace amounts of CO2. Therefore, CO2 was not considered for the calculation of either propylene conversion or PO selectivity in this work and for the data reported previously [5]. The minimum observable CO2 signal in the system used for this work was 0.18 vol% in the gas stream, corresponding to 0.62% conversion of propylene to CO2. The reported PO selectivity is an upper bound with a potential maximum error of 40%, which is estimated via assuming that the amount of CO2 generated is ~0.18 vol%. This means that a reported selectivity of 90% could correspond to an actual selectivity between 50% and 90%. However, we note that the PO selectivity of the Au/TS-1 with the gold loading ~0.05 wt% has been shown to be greater than 80% [4,6]. Carbon balances without taking CO2 into consideration, defined as, (moles of C measured from the reactor effluent (which is equal to 3 × (propylene + PO + Pr + Ac + An) + 2 × ethanol)/moles of C in the feed (which is equal to 3 × propylene), were found to be ~95%.
Table 1

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>BET surface area (m² g⁻¹)</th>
<th>Pore volume (cm³ g⁻¹)</th>
<th>Ti content (wt%)</th>
<th>Au content (wt%)</th>
<th>Au/Ti (molar ratio)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S-1</td>
<td>375 ± 16</td>
<td>0.231</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>TS-1(77)</td>
<td>418 ± 12</td>
<td>0.265</td>
<td>1.02</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>TS-1(99)</td>
<td>403 ± 11</td>
<td>0.245</td>
<td>0.80</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>TS-1(127)</td>
<td>423 ± 11</td>
<td>0.257</td>
<td>0.62</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>S-1</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>S-1/TS-1</td>
<td>355 ± 13</td>
<td>0.233</td>
<td>2.00</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>0.054Au/S-1/TS-1</td>
<td>0.22</td>
<td>0.045</td>
<td>0.05</td>
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</tr>
<tr>
<td>0.054Au/S-1/TS-1-repeate</td>
<td>0.22</td>
<td>0.054</td>
<td>0.06</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

N/A: not applicable.
ND: not determined.

a The number in the parenthesis represents the Si/Ti molar ratio.
b Determined by EDS analysis.
c Determined at P/P₀ = 0.97.
reaction due to the Au–Ti proximity near the external surface of the TS-1 seed. No hysteresis loop in the relative pressure ($P/P_0$) range of 0.2–0.6, characteristic of multilayer adsorption occurring inside a mesopore, was found in the N₂ adsorption/desorption isotherms of 0.054Au/S-1/TS-1, however, and this indicates the absence of mesopores in 0.054Au/S-1/TS-1, even after the gold deposition. The hysteresis hoop observed at high relative pressure ($P/P_0$) of 0.85–0.99 for 0.054Au/S-1/TS-1 can be assigned to large pores in the intercrystalline space [29]. Those pores are about 8–14 nm in diameter as calculated according to the Kelvin equation (parameters used for the mesopore diameter calculations are available in the SI). Such large pores would have easily been observed by TEM if they had been inside the crystallites, but none were found, indicating the absence of the mesopores in either S-1/TS-1 or 0.054Au/S-1/TS-1.

Fig. 7 shows the DRUV–vis spectrum of the S-1/TS-1, which reflects the local coordination environment of titanium inside the TS-1 seed. The lack of absorption above 330 nm shows that there was no formation of anatase-like extraframework Ti. A sharp absorption peak around ~220–230 nm indicates that most of the titanium was incorporated into the framework and present in tetrahedral coordination, as expected for TS-1 [5].

The most important feature of the S-1/TS-1 material is the Ti spatial gradient. Our aim was to totally cover the external surface of the TS-1 seed with S-1, ensuring there was no Ti on the external surface of the S-1/TS-1 particles. The bulk elemental composition of the S-1/TS-1 was analyzed by EDS analysis on a selected composite particle, as shown in Fig. 8. In addition to silicon and oxygen, a trace amount of titanium was also detected. The weak titanium signal was consistent with the thick S-1 layer in the S-1/TS-1, which resulted in the TS-1 seed occupying ~12.5% of the total volume of the composite particles. A surface-sensitive technique was also used to examine the surface elemental composition. Fig. S9 in the SI shows an XPS spectrum, in the Ti 2p region, for fresh 0.054Au/S-1/TS-1. No Ti signal was detected, indicating that the entire external surface of the TS-1 seed was covered by S-1 and that the gold deposition process did not leach out the Ti and/or re-precipitate Ti on the external surface of fresh 0.054Au/S-1/TS-1. We note that no Ti signal was detected on the spent 0.045Au/S-1/TS-1 sample as well. XPS analysis was also performed on fresh 0.054Au/S-1/TS-1, which had been sputtered by helium for 5 min, and still no Ti signal was detected (XPS spectrum not shown). The sensitivity of this measurement will be analyzed in more detail later in the discussion.

TEM analysis (Fig. 9a) showed no visible gold particles on fresh 0.054Au/S-1/TS-1, which indicates that the gold species were highly dispersed in the S-1/TS-1. However, a few gold particles with size between 2 and 4 nm were observed for spent 0.054Au/S-1/TS-1 after reaction at 200 °C for ~22 h, as shown in Fig. 9b and c. We note that total visible gold particle density (# nm⁻², calculated from the TEM images in which gold particles could be observed) of the spent 0.054Au/S-1/TS-1 (2.6 × 10⁻⁴ # nm⁻²) was four times lower than that of the spent 0.045Au/S-1/TS-1 (1.1 × 10⁻³ # nm⁻², with average gold particle size ~2.47 ± 0.76 nm and PO rate ~120 gPO h⁻¹ kgcat⁻¹) after reaction at 200 °C for ~10 h with comparable gold loading, as shown in Fig. 9d. This observation suggests that the gold
particle size distribution might be affected by the Ti spatial distribution in the support since gold has been suggested to preferentially anchor at Ti sites [5,6,9]. Therefore, more gold species might be present inside the Au/S-1/TS-1 as compared to the regular Au/TS-1 because there is no Ti to provide the anchor points in the outer S-1 layer of the Au/S-1/TS-1 samples.

3.3. Kinetics of PO formation over Au/S-1/TS-1

Fig. 10 shows PO rate \((g_{PO} \text{ h}^{-1} \text{ kg}_{\text{Cat}}^{-1})\) for the Au/S-1/TS-1 samples and the Au/S-1 samples with different gold loadings at \(\sim 200^\circ\text{C}\). The PO rates of 0.045Au/S-1/TS-1 \((\sim 26 \text{ g}_{\text{PO}} \text{ h}^{-1} \text{ kg}_{\text{Cat}}^{-1})\) and 0.054Au/S-1/TS-1 \((\sim 30 \text{ g}_{\text{PO}} \text{ h}^{-1} \text{ kg}_{\text{Cat}}^{-1})\) were at least 50 times higher than that of 0.028Au/S-1 \((\sim 0.5 \text{ g}_{\text{PO}} \text{ h}^{-1} \text{ kg}_{\text{Cat}}^{-1})\). The significant difference in the PO rate per gram of catalyst between Au/S-1/TS-1 and Au/S-1 indicates the existence of Au–Ti proximity in the Au/S-1/TS-1 samples, which has been suggested to be essential for the high PO rate performance [2,17,18]. Although the loading of gold on the coated catalyst is twice that of the S-1 sample to which it is compared, the gold loading itself is not the cause of the significant difference in the rate. An attempt to further increase the gold loading of Au/S-1 to 0.051 wt%, comparable to that of the Au/S-1/TS-1 samples, only enhanced the PO rate per gram of catalyst to \(\sim 1.5 \text{ g}_{\text{PO}} \text{ h}^{-1} \text{ kg}_{\text{Cat}}^{-1}\) at \(\sim 200^\circ\text{C}\). The PO rate per gram of catalyst for another individual 0.052Au/S-1 sample was found to be around 1.3 \text{ g}_{\text{PO}} \text{ h}^{-1} \text{ kg}_{\text{Cat}}^{-1}\) at \(\sim 205^\circ\text{C}\). Furthermore, the influence of the potential Ti contamination from the Teflon liners on the S-1 support and its corresponding impact on the PO rate per gram of catalyst was found to be smaller than 0.5 \text{ g}_{\text{PO}} \text{ h}^{-1} \text{ kg}_{\text{Cat}}^{-1}\) at \(\sim 200^\circ\text{C}\), as indicated from the rate comparison between 0.051Au/S-1 and 0.055Au/S-1/ap samples. The corresponding PO rate versus time-on-stream plots for the three individual Au/S-1 samples are available in Figs. S4–S7. We also note that the acid pretreatment (ap), which is used to remove possible residual Ti on the S-1 from contamination, did not have noticeable effect on the crystalline structure of the S-1, as evidenced by the similar XRD signal intensities for both S-1/ap and a reference TS-1(99) sample (Fig. S8). To evaluate the importance of this result, we look first at whether the observed rate could be driven by Au not proximate to Ti.

The PO rate per gram of catalyst for a physical mixture of \((\sim 0.5 \text{ g each})\) 0.019Au/S-1 and TS-1(65) was found to be at the level of \(0.3–0.5 \text{ g}_{\text{PO}} \text{ h}^{-1} \text{ kg}_{\text{Cat}}^{-1}\), which suggests that even if H\(_2\)O\(_2\) is formed on Au/S-1, it does not migrate far enough before decomposition to produce PO on the TS-1(65) [discussed further below].

Next, we consider the question of whether gold not in the Ti-1 pores could have been close enough to Ti sites to account for the observed rate. We recall from the discussion above that the whole S-1/TS-1 particle possesses the MFI structure (by SAED analysis), which ensures a well-defined nanopore system with \(\sim 5.5 \text{ Å}\) pore diameter in the S-1/TS-1 support and the supported Au catalyst. Furthermore, the lack of mesopores evidenced in the N\(_2\) isotherm suggests that there was not a significant opportunity for gold particles larger than 0.55 nm to be proximate to the Ti in the TS-1 seed.

Finally, we consider the possibility that Ti may have migrated to the external surface of the S-1/TS-1 structure to provide Ti sites that could be proximate to large gold particles on the external surface of the catalyst. The XPS results already discussed show that no Ti was detected on the Au/S-1/TS-1 samples by this surface sensitive technique, suggesting that there was no possibility for Au–Ti proximity on the external surface of the Au/S-1/TS-1. Because of the high gold atom efficiency \((\sim 500 \text{ g}_{\text{PO}} \text{ h}^{-1} \text{ kg}_{\text{Cat}}^{-1})\) reported at very low gold loadings \((\sim 0.01 \text{ wt%})[5]\), significant rate per gram of catalyst can be provided by a relatively small number of sites. Thus, it is useful to probe the sensitivity of the XPS measurement to give an upper bound on the rate that could be associated with the presence of Ti in an amount too low to give an XPS signal. We assume that the amplitude of noise in the XPS signal (indicated by a black arrow in Fig. S9) represents the peak height of the maximum Ti signal \((\sim 3 \text{ cps})\) on the external surface of the fresh 0.054Au/S-1/TS-1. Note that we have also assumed that the peak shapes will be the same and that peak areas are proportional to the heights of the peaks. The peak area ratio between the Si \((\sim 2794 \text{ cps})\) signal and the Ti
signal (~3 cps) for the fresh 0.054Au/S-1/TS-1 is ~931. Furthermore, the peak area ratio between the Si signal (~2207 cps) and Ti signal (~87 cps) was found to be ~25 on the external surface of the spent 0.16Au/TS-1(121) (Si and Ti signals are shown in Fig. S10 in the SI). Given that the surface Si/Ti molar ratio (which is proportional to the peak area ratio between the Si and Ti signals) for the spent 0.16Au/TS-1(121) was ~166, the estimated surface Si/Ti molar ratio for the 0.054Au/S-1/TS-1 can be calculated and was found to be ~6180 (~931 × 166/25). If we further assume that all the reaction takes places only over the trace amount of the Ti sites on the external surface of the TS-1 and that the gold clusters inside the TS-1 nanopores are totally inactive, we can compute the turnover frequency (TOF) per surface Ti site by assuming all the reaction takes places on the external surface. The surface Ti content of the 0.054Au/S-1/TS-1 is about 37 (6180/166 = ~37) times lower than that of the spent 0.16Au/TS-1(121), so we can scale the TOF per surface Ti site obtained from the spent 0.16Au/TS-1(121) sample, and the corresponding PO rate (gPO h$^{-1}$ kg$_{Cat}^{-1}$) of the Au/S-1/TS-1 sample is ~4 gPO h$^{-1}$ kg$_{Cat}^{-1}$ (~160/37 = ~4.3 gPO h$^{-1}$ kg$_{Cat}^{-1}$). This is very likely to be a significant over-estimate because it assigns all the activity to the external surface. Nevertheless, this PO rate (~4 gPO h$^{-1}$ kg$_{Cat}^{-1}$), computed based on the assumptions that there may exist trace amounts of surface Ti on the fresh 0.054Au/S-1/TS-1 that were not detected by XPS and that the gold clusters inside the TS-1 nanopores were totally inactive, is still about an order of magnitude lower than the PO rate observed for the Au promoted, S-1-coated catalyst in this work. Therefore, the experimental results,

Fig. 4. TEM images of zeolite structures coupled with their corresponding SAED patterns along [010] for (a) TS-1 seed and (b) S-1/TS-1. Inset: The systematically absent peaks on the simulation [26,27] (shown as ‘x’) are present on the actual SAED pattern (indicated by gray arrows) due to double-diffraction.

Fig. 5. HRTEM image of marked area of the S-1/TS-1 (in the inset B, the scale bar represents 50 nm), which shows the continuous atom registry of the coated S-1 in spite of the irregular termination of the S-1 layers. Inset A shows the FFT of the S-1/TS-1 structure.

Fig. 6. N$_2$ adsorption/desorption isotherm of S-1 and 0.054 Au/S-1/TS-1. The N$_2$ adsorbed and desorbed (y axis) for 0.054Au/S-1/TS-1 were shifted by +50 cm$^3$ g$^{-1}$ for clarity. No hysteresis loop was found between $P/P_0$ = 0.2–0.6, indicating the absence of mesopores, and the similar amount of nitrogen adsorbed in both Au/S-1/TS-1 and S-1 suggests that the nanopores inside the S-1/TS-1 were not blocked by the irregular coating of the S-1 layers.
supported by this simple calculation, suggest that gold clusters small enough to be inside the TS-1 pores are the source of high reaction rate for the production of PO.

Fig. 11a indicates that the PO rate for 0.054Au/S-1/TS-1 showed good stability for at least 20 h, even though there was an initial decay in the PO rate at the first few hours. The corresponding PO selectivity, as well as the H₂ selectivity of 0.054Au/S-1/TS-1 as a function of reaction temperature and/or reaction time, is shown in Fig. 12 (the corresponding propylene conversion, H₂ conversion, and the selectivity for the other oxygenates are available in Figs. S1–S3 in the SI). The PO selectivity was about 89% at ~202 °C, which is consistent with the value of our regular Au/TS-1 with similar Au and Ti loadings [5]. The increased PO selectivity at decreased reaction temperature, shown in Fig. 12, implies that the formation rate of other oxygenates from either the isomerization or cracking of PO increased as temperature increased.

In addition to the propylene epoxidation, the formation of propane via hydrogenation of propylene in the mixture of O₂ and H₂ over the Au–Ti catalyst system has also been reported in the literature [30,31]. Although the reaction mechanism for the switch between the hydrogenation and epoxidation of propylene in the presence of H₂ and O₂ has been studied, it is still under debate. Nijhuis and coworkers proposed that the state of the Ti sites on the support is relevant to propylene hydrogenation [30]. On the other hand, Haruta and coworkers proposed that the presence of alkali determines the reaction pathways; specifically, that the presence of alkali (>100 ppm) can switch off propylene hydrogenation over
Au clusters smaller than 2 nm [31]. In the work presented here, the amount of propane measured from the reactor effluent for the 0.054Au/S-1/TS-1 sample was found to be negligible at reaction temperature \(200^\circ\text{C}\), which might be explained by presence of the residual Na inherent from using Na\(_2\)CO\(_3\) as the precipitation agents during DP [31]. We note further that while propane formation over Au/TS-1 was either not reported or not produced in the earlier work by Oyama’s and other research groups [17,32,33], some propane, with selectivity \(\sim 15\%\) at \(200^\circ\text{C}\), was recently reported by Oyama’s group for Au/TS-1 prepared at similar conditions (fresh sample prior cyanide leaching) [22]. Similarly, no formation of propane was reported for the Au/Ti–SiO\(_2\) catalysts prepared by Qi et al. [34], while a significant propane formation was reported by Chen et al. [30], even though the catalyst was post-impregnated with Na. Thus, the precise source of high propane selectivity is not clear at present but certainly merits further study.

As for the H\(_2\) selectivity of 0.054Au/S-1/TS-1, it was found to be about 5–10\% lower than that of the regular Au/TS-1 with similar Au and Ti loadings [5]. The decreased H\(_2\) selectivity can be explained by inefficient usage of hydrogen peroxide generated by the gold clusters distributed in the S-1 layer, but not proximate to Ti. Additionally, there appears to have been formation of extra hydrogen combustion sites occurring during the reaction, as evidenced by the almost four times decrease in the H\(_2\) selectivity at \(145^\circ\text{C}\) versus \(200^\circ\text{C}\) of reaction time. It has been reported that the H\(_2\) combustion rate is a function of the gold particle size in gold catalysts, and that larger gold particles (>2 nm) were found to
promote H₂ combustion in Au/mesoporous titanosilicate system [35]. The decreased H₂ selectivity as the reaction time increased might be due to the formation of the larger gold particles, which would create extra sites for H₂ combustion.

The measured apparent activation energy of 0.054Au/S-1/TS-1 for the PO reaction was about ~28 kJ mole⁻¹ (Fig. 11b), which is similar to the values (~30 kJ mole⁻¹) previously reported for regular Au/TS-1 catalysts [6], while that for three individual ~0.05Au/S-1 samples (the corresponding Arrhenius plots are shown in Figs. S4–57) was found to be only ~10–15 kJ mole⁻¹, suggesting that the kinetic behavior observed in the Au/S-1/TS-1 cannot be dominated by the Au clusters in the S-1 layer. Moreover, similar activation energies between Au/TS-1 catalysts and 0.054Au/S-1/TS-1 imply similar reaction mechanisms and/or the similar reaction active sites. The fact that the kinetic behavior of the gold clusters inside the nanophase Au[S-1/TS-1] could not be distinguished from that for regular Au/TS-1 suggests the small gold clusters inside the TS-1 nanophase are likely active sites.

3.4. Location of the gold active sites

Xu et al. [16] have reported similar studies to the ones reported here. They prepared MCM-41 type mesoporous silica-coated TS-1 material (mesoSiO₂ shell/TS-1 core), used it to support gold nanoparticles, and tested the resulting catalyst for the PO reaction at 150 °C. The highest PO rate among their samples (sample ID: TS-1-60@meso-SiO₂-3.0TEOS with gold loading ~0.2 wt%) gave a rate of ~23 gpo h⁻¹ kgCat⁻¹ at 150 °C (propylene conversion ~2.6%, PO selectivity ~94.4%, space velocity = 4000 mL h⁻¹ gCat⁻¹). Extrapolating that rate to 200 °C by assuming an activation energy ~30 kJ mole⁻¹ [6] gives a rate of ~57 gpo h⁻¹ kgCat⁻¹. Our PO rate of 0.054Au/S-1/TS-1 (~30 gpo h⁻¹ kgCat⁻¹) is lower, but this difference can be attributed to the much thicker S-1 layer coating (silica shell thickness ~160 nm, the diameter of the S-1/TS-1 sphere ~560 nm) in our S-1/TS-1 as compared to the mesoporous SiO₂ coating (silica shell thickness ~55 nm, the diameter of the meso-SiO₂ shell/TS-1 core ~330 nm) in their samples. The dilution of the active catalyst by the inactive silica lowers the rate per gram of catalyst. The assumption that one Ti site can accommodate one gold atom leads to the conclusion that TS-1 with a Ti content <12.5% and ~29.6% of the total volume of Si/Ti <0.8 wt% (which corresponds to Si/Ti molar ratio ~100) can accommodate a gold loading as high as ~3.3 wt%. Considering that there are ample Ti sites to accommodate the gold clusters and the fact that Au and Ti need to be proximate to give a significant PO rate, the PO rate should be normalized by the amount of TS-1 instead of the total amount of catalyst in the silica-coated samples discussed above. If we account for the thickness of the silica coating, the TS-1 only occupied ~12.5% and ~29.6% of the total volume in the S-1/TS-1 and the mesoSiO₂ shell/TS-1 core samples, respectively. The PO rate of Au/S-1/TS-1 renormalized per gram of TS-1 would be ~240 gpo h⁻¹ kgTS⁻¹, which is comparable to that of TS-1-60@meso-SiO₂-3.0TEOS at ~192 gpo h⁻¹ kgTS⁻¹. The significant PO rate observed in the TS-1-60@meso-SiO₂-3.0TEOS might also serve as the evidence that gold clusters inside the nanophase of the TS-1 could be active for the PO reaction because there was little restriction for gold species to migrate into the TS-1 core in the TS-1-60@meso-SiO₂-3.0TEOS. On the other hand, the gold particles with size 2–3 nm, confined in the coated mesoporous silica matrix, could be right on the external surface of the TS-1 core and create potential active Au–Ti sites there.

Xu and coworkers [16] proposed that H₂O₂ could be generated at Au sites in situ in the silica shell and then sequentially diffuse to the Ti sites in the TS-1. This hypothesis could also be true in our
case, although the gold particles would have to be in the 0.5 nm size range. In that case, the observed high PO rate in the Au/S-1/TS-1 samples could not be attributed only to the existence of the Au–Ti proximate sites inside the TS-1 nanopores. How long the H₂O₂ intermediate can travel/diffuse before it is decomposed remains unclear, however. A Temperature-Programmed Decomposition (TPD) experiment on the titanium-peroxide species in a TS-1 sample showed a desorption peak at ~130 °C, which implies (1) low stability of the adsorbed peroxide species and (2) low possibility of propylene sequentially reacting with peroxide species that have to migrate to Ti sites at the reaction temperature of 200 °C [36]. The relatively thick S-1 layer and 200 °C reaction temperature both challenge the H₂O₂ transport mechanism. To address the H₂O₂ diffusion issue further, we carried out physical mixture experiments to assess the possibility of the high PO rate being caused by the sequential reaction steps in which H₂O₂ is first generated on the Au sites and then transported to the Ti site for the PO reaction. It has been reported, both in theoretical computations and the experiments, that gold catalysts can produce hydrogen peroxide [8,10–12,37]. Therefore, we prepared 0.019Au/S-1, to serve as the H₂O₂ production sites, and ran the PO reaction over a catalyst prepared by physically mixing 0.51 g of 0.019Au/S-1 with the 0.52 g TS-1(65) to test whether any significant PO rate could be obtained. Fig. 10 shows the corresponding PO rate performance of this catalyst. Its PO rate of ~0.3 gPO h⁻¹ kg⁻¹ Cat at 200 °C was much lower than the observed PO rate for the Au/S-1/TS-1 samples (~30 gPO h⁻¹ kg⁻¹ Cat). A similar experiment in which 0.16 g of Au/rutile with gold loading ~2.5 wt%, instead of 0.019Au/S-1, was mixed with 1.63 g of TS-1(65) gave an undetectable PO rate at either 82 °C or 172 °C, even though trace amounts of other oxygenates were detected. These experimental results suggest the lifetime of the hydrogen peroxide at the high temperature of 200 °C is very short. In fact, our previous DFT calculations [38] also showed that the activation energy for the formation of Ti-OOH on the Ti-defect sites which are in proximity to Au clusters is higher (~32 kJ mol⁻¹) than that on the bare Ti-defect sites (~17 kJ mol⁻¹), which suggests that the sequential reaction mechanism is kinetically inhibited when Au and Ti are in proximity.

It is challenging to identify whether the gold clusters inside the nanopores are the major contributor to the PO rate because the quantification of how much gold was in intimate contact with the Ti in the TS-1 seed is not possible. Similarly, a precise rate comparison between Au/S-1/TS-1 and the regular Au/TS-1 samples is difficult since the ability of gold species to reach the Ti sites is different in pure TS-1 versus S-1/TS-1 (i.e., the Ti gradient is different), which in turn, might result in different numbers of effective gold active sites. If we assume that (1) the H₂O₂ diffusion mechanism makes no contribution to the PO rate and that the PO rate all comes from the proximate Au–Ti sites and (2) the formation of the Au–Ti active site is independent of the S-1 layer in Au/S-1/TS-1, then the PO rate normalized per gram of TS-1 is ~240 gPO h⁻¹ kg⁻¹, for 0.054Au/S-1/TS-1 (the Si/Ti molar ratio for the TS-1 seed is ~40) compared to ~140 gPO h⁻¹ kg⁻¹ for ~0.055Au/TS-1(100) and ~60 gPO h⁻¹ kg⁻¹ for ~0.055Au/TS-1(65). This substantially higher PO rate per gram of TS-1 in Au/S-1/TS-1, compared to either Au/TS-1(100) or Au/TS-1(65) at similar gold loadings, might be due to more gold species available inside the TS-1 nanopores (more Au–Ti active sites) during the reaction because of either the long diffusion path through the S-1 layer for Au to migrate to form large particles on the outer surface or Ti in the TS-1 seed serving as a sink for attraction of the gold species. The ability of the S-1/TS-1 support to better anchor Au in the TS-1 core is suggested by the smaller density of visible gold particles observed for the spent 0.054Au/S-1/TS-1 versus the spent 0.045Au/TS-1(127) as discussed above. Moreover, the PO rate (per gram of catalyst) has also been found to be a function of the Ti content [5]. The Au/TS-1 with higher Ti content showed lower PO rate per gram of catalyst than the one with lower Ti content, even though both catalysts had similar gold loadings [5]. We attributed this phenomena to the possible existence of extraneous TiOx and/or small TiOx clusters in the TS-1 with higher Ti content. Considering that the Si/Ti molar ratio in the TS-1 seed (~40) is lower than that in TS-1(65), the much higher PO rate per gram of TS-1 for 0.054Au/S-1/TS-1 than 0.055Au/TS-1(65) (~240 versus ~60 gPO h⁻¹ kg⁻¹) is even more unusual than expected. In addition to the possibility of more gold species available inside the TS-1 nanopores as discussed above, less extraneous Ti was present in the Au/S-1/TS-1, as evidenced by the much sharper DRUV–vis absorption in the S-1/TS-1 compared to that in the Au/TS-1(65) (Fig. 7), which can also benefit the PO rate. In any case, the much higher PO rate per gram of TS-1 in Au/S-1/TS-1 suggests that the gold clusters inside the TS-1 nanopores are viable candidates for the dominant active site.

4. Conclusions

We have hypothesized that the gold clusters inside the TS-1 nanopores can be active in the PO reaction, based on our previous experimental observations [6,7] and DFT calculations [8,9]. The experimental results presented here show that gold supported on a TS-1 seed thoroughly coated with a relatively thick, continuous S-1 layer, had at least 20 times higher PO production rate (gPO h⁻¹ kg⁻¹), compared to that of an Au/S-1 sample with a similar gold loading ~0.05 wt% and showed a rate of ~240 gPO h⁻¹ kg⁻¹, higher than expected for the TS-1 seed alone. This is the first direct experimental evidence showing that the gold clusters inside the TS-1 are active and that they can generate the dominant active sites for the PO reaction.

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Appendix A. Supplementary material

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References