

Enhancement of Au capture efficiency and activity of Au/TS-1 catalysts for propylene epoxidation

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Abstract

A method for enhancing the useful Au content in Au/TS-1 catalysts for vapor-phase propylene epoxidation is reported. Exposure of calcined TS-1 support to 1 M NH_4NO_3 at 80 °C, followed by vacuum drying, produced a modified TS-1 support material. Deposition precipitation of gold on these modified TS-1 supports resulted in a fourfold increase in Au capture efficiency and produced catalysts with 5–10% conversion of propylene with 75–85% selectivity for PO, at 200 °C and a space velocity of 7000 $\text{ml h}^{-1} \text{g}_{\text{cat}}^{-1}$. In this system, 10% conversion and 76% selectivity amount to a rate of 134 $\text{g}_{\text{PO}} \text{h}^{-1} \text{kg}_{\text{cat}}^{-1}$. An optimal Au content that is support dependent is observed for these catalysts.

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1. Introduction

The discovery by Haruta and co-workers [1] that nano-scale gold particles on titania supports provide a highly selective (~ 99%) route to vapor-phase propylene oxide production, with the use of a mixture of propylene, oxygen, and hydrogen under ambient pressure, has been a significant breakthrough in heterogeneous catalysis. A direct, single-step epoxidation of propylene to propylene oxide (PO) has both practical and fundamental implications. Although the high selectivity shown for PO production in propylene/oxygen/hydrogen mixtures over Au/Ti catalysts is an important step toward a new process, further understanding of the catalytic functions is needed to guide improved catalytic formulations for partial oxidation of molecules containing allylic hydrogen.

Subsequent studies by Haruta and in other laboratories around the world have confirmed the high selectivity of

these systems [2,3]. Speculation and circumstantial evidence that the role of hydrogen is to form HOOH, which is the electrophilic oxidant, has recently been supported by direct observation of HOOH formation on Au/TiO₂ systems [4]. Careful TEM studies have suggested that 2–5-nm Au particles have special properties for PO production [1]. Smaller particles have been seen to make propane in the propylene/oxygen/hydrogen reaction environment, whereas larger Au particles make CO₂. Early work in our laboratory [5] and that of others [2,6,7] have shown the activity and selectivity of Au/Ti PO catalysts to be very sensitive to the nature of the support. Au on rutile is inactive. Au on anatase or amorphous TiO₂ is active, but Au on monolayers and submonolayers of TiO₂ on silica is more active. We have concluded from this work that isolated, tetrahedrally coordinated Ti is most effective, and that led us to TS-1 as the support of choice for our studies.

The low site density is a key problem with these Au/TS-1 catalysts. The selectivity is up to commercial standards, but the activity is not. The ability to control the deposition of Au on TS-1 during deposition precipitation could allow en-

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hancement of the site density, particularly as more is learned about the nature and position of the active Ti sites. A study of the deposition precipitation (DP) parameters for Au deposition on TS-1 has shown that, at a pH of 9–10, 1–3% of the available Au in the solution was deposited on conventional TS-1 supports [8].

In this work, a newly discovered ammonium nitrate enhancement of the useful Au content in Au/titanium-silicalite-1 (TS-1) propylene epoxidation catalysts is reported. The Au capture efficiency of the support during deposition precipitation has been increased remarkably by the ammonium nitrate treatment, permitting the use of very low concentrations of the rather expensive Au precursor ($\text{HAuCl}_4 \cdot x\text{H}_2\text{O}$). The Au capture efficiency is defined as the fraction of Au from the $\text{HAuCl}_4 \cdot x\text{H}_2\text{O}$ precursor solution that is deposited on the support material during deposition precipitation. Au loadings have been enhanced while the average particle diameter of the observed gold is maintained at 5–6 nm. Furthermore, we have compared Au/TS-1 catalysts, with and without NH_4NO_3 pretreatment of the same batch of TS-1 support material and with similar Au loading, to show the enhancement in activity due to the NH_4NO_3 pretreatment.

2. Experimental

2.1. Synthesis and characterization of TS-1 supports

A method based on a non-ionic surfactant, polyoxyethylene 20-sorbitan monolaurate (Tween 20, enzyme grade; Fisher Scientific), outlined by Khomane et al. [9], was used for the preparation of the TS-1 support material. The TS-1 support materials prepared by this method were calcined in a 20% O_2 /balance He mixture for 12 h at 808 K to burn out the template. The ramp rate of the calcination furnace was set at 0.7 K min^{-1} to reach a temperature of 808 K.

The Au and Ti loadings were determined with a Perkin-Elmer 3110 atomic absorption (AA) spectrometer. We prepared samples for AA by digesting 0.1 g of catalyst in 2 ml of aqua regia and 1 ml of HF, in a polypropylene flask, for a period of 7 days and finally diluting the solution to 50 ml. BET surface area analysis through N_2 adsorption isotherms was done with a Micromeritics ASAP 2000 surface area analyzer after sample out-gassing under vacuum at 523 K for a period of 6 h. S_{BET} gave an indication of the total surface area of the catalyst. In addition, all catalyst supports were checked for crystallographic phase by XRD with a Siemens D500 diffractometer and $\text{Cu-K}\alpha$ X-rays.

Diffuse reflectance spectroscopy (DRUV-vis) was used to observe the existence of TiO_2 phases and extraframework Ti in the TS-1 supports. DRUV-vis spectra of the powder samples were obtained with a Varian (Cary 5000) spectrophotometer with a Harrick-Scientific Praying-Mantis diffuse reflectance accessory. Samples were diluted to 10:1

with MgO (perfect reflector) and lightly ground with a mortar and pestle before they were loaded into the instrument.

The average TS-1 particle diameters (D_s) and the average Au particle diameter (D_m) were determined after analysis of a minimum of 35 particles from TEM (JOEL 2000 FX at 200 keV) micrographs and with UTHSCSA Image Tool version 3.0 image analysis software. All Au particle sizes presented are from post-reaction (steady-state kinetic analysis) TEM images, since no visible particles were present in fresh catalysts.

2.2. Post-synthesis treatments and Au deposition

The modified TS-1 support material was formed by the post-synthesis treatment of the calcined TS-1 with aqueous NH_4NO_3 . In a typical treatment, 1.0 g of calcined TS-1 support material was added to 60 ml of 1 M NH_4NO_3 solution in a 100-ml beaker, and the solution mixture was stirred for 15 h at 80°C . After the contents in the beaker were cooled to room temperature, the solid material was centrifuged out, washed in 80 ml of DI water, centrifuged again, and vacuum dried at room temperature for 12 h.

We accomplished DP of Au onto the untreated support materials by stirring 1 g of calcined TS-1 support material in 50 ml of $0.8\text{--}3.0 \text{ mg ml}^{-1}$ $\text{HAuCl}_4 \cdot x\text{H}_2\text{O}$ (purity 99.999% metal basis) solution at room temperature for 2–3 h. The solution pH was maintained at 9 by the addition of a few drops of 1 M Na_2CO_3 . To bring about DP on the modified supports, we stirred 1 g of modified support material in 50 ml of $0.4\text{--}0.6 \text{ mg ml}^{-1}$ $\text{HAuCl}_4 \cdot x\text{H}_2\text{O}$ solution (pH ~ 9) at room temperature for 2–3 h. In both cases, the solid catalyst was centrifuged out, washed in 40 ml of DI water, centrifuged again, and finally vacuum dried at room temperature for 12 h. Catalysts have been identified throughout the paper as C_Au wt%_Ti wt%, and the letter N has been used to indicate catalysts that were treated with NH_4NO_3 .

2.3. Catalyst activity measurements

Reaction rates, analyzed after 4–6 h of steady-state activity, were measured with a half-inch vertical stainless-steel reactor housed in a Lindberg Solar Basic furnace. Reaction gas flows were measured with bubble flow meters, and products were analyzed with a Varian 3740 gas chromatograph with an automated sampling valve. Oxygen and carbon dioxide gases were analyzed with a Chromosorb 102 packed column (Supelco; length 1.83 m, diameter 3.81 mm) and a thermal conductivity detector (TCD), while the partially oxidized products were analyzed with a fused silica Supelcowax 10 capillary column (Supelco; length 60 m, diameter 0.53 mm, film thickness $1.0 \mu\text{m}$) with a flame ionization detector (FID). Reaction temperatures were monitored with a stainless-steel-jacketed Type K thermocouple inside of the catalyst bed. Catalytic reactions were run in a 10/10/10/70 vol% reactant mixture of hydrogen (99.9995%), oxygen (99.9995%), propylene (99.9%), and helium (99.9995%) at a

space velocity of $7000 \text{ ml h}^{-1} \text{ g}_{\text{cat}}^{-1}$. Catalysts were sieved to 40–60 mesh before kinetic tests to ensure a uniform particle diameter of 250–400 μm . Steady-state kinetic measurements were performed at 140, 170, and 200 $^{\circ}\text{C}$, with each catalyst remaining at each temperature window for 6–12 h. Catalyst activation was carried out on-stream with heating from room temperature to 200 $^{\circ}\text{C}$ for a period of 5 h, at a heating rate of 0.6 K min^{-1} , in the reaction gas mixture. A typical temperature sequence is shown in Fig. 3.

3. Results and discussion

A comparison of the rate of PO production for NH_4NO_3 -treated versus untreated catalyst on the same TS-1 support material with varying Au loadings is shown in Fig. 1. The same batch of support material was used for both sets of catalysts to remove effects of the primary support as an influence on catalyst performance. Hence all of these supports share the same Ti loading, the same TS-1 crystallite sizes, and other support characteristics. The initial $\text{HAuCl}_4 \cdot x\text{H}_2\text{O}$ solution concentrations and total time duration of DP have been varied in order to vary the Au loadings. The initial concentration of $\text{HAuCl}_4 \cdot x\text{H}_2\text{O}$ solution for NH_4NO_3 -treated supports for this series of catalysts was varied between 0.4 and 0.6 mg ml^{-1} , and the initial concentration of $\text{HAuCl}_4 \cdot x\text{H}_2\text{O}$ solution for untreated supports was varied between 0.8 and 3.0 mg ml^{-1} . The difference was necessary to obtain similar Au loadings.

The Ti loading of the TS-1 support used for all of the catalysts in Fig. 1 was 2.2 wt% (Si/Ti ~ 36), and the average TS-1 crystal size was $360 \pm 40 \text{ nm}$. The BET surface area of the TS-1 support material before the NH_4NO_3 treatment was

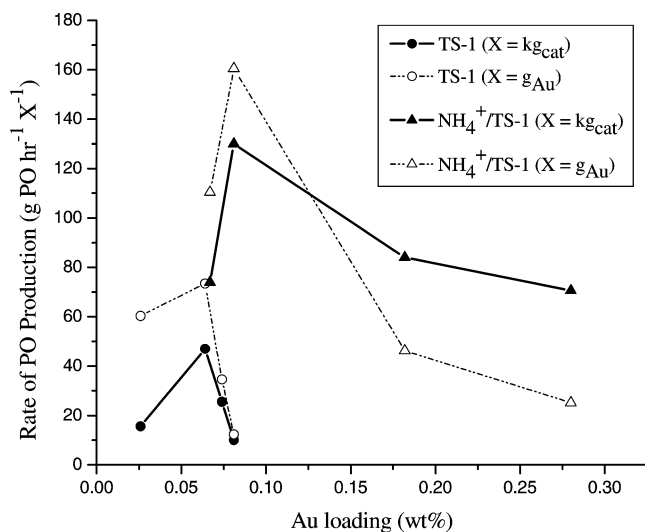


Fig. 1. PO production rates for NH_4NO_3 -treated and untreated catalysts for the same batch of TS-1 support material. The PO production rates (average rates) are reported after 4–6 h of steady state activity at 200 $^{\circ}\text{C}$. Open symbols represent the rate per g of Au and the closed symbols represent the rate per kg of catalyst. The lines joining the data points are included only as a guide for the eye.

$411 \pm 7 \text{ m}^2 \text{ g}^{-1}$ and remained unchanged after the NH_4NO_3 treatment. XRD patterns and DRUV-vis spectra for the standard and NH_4NO_3 -treated supports are shown in Figs. 2a and b. The XRD patterns shown in Fig. 2a are consistent with that of TS-1 in the literature [9,10]. These TS-1 support materials have a high order of crystallinity, as indicated by the relatively flat baseline in Fig. 2a. The DRUV-vis spectra, shown in Fig. 2b, exhibit strong absorptions at 218 nm. This band is attributed to electronic transitions between O^{2-} and Ti^{4+} in isolated framework Ti^{IV} centers in a tetrahedral environment. The absence of an absorption band at 270–370 nm confirms that no anatase or extraframework Ti is present in these samples [10].

The results, shown in Fig. 1, indicate that the Au loading on NH_4NO_3 -treated supports can be varied over a wide range compared with the untreated support materials. Fig. 1 also shows a marked increase in PO formation rate for NH_4NO_3 -treated catalysts compared with untreated catalysts with similar Au loadings (closed symbols/solid lines).

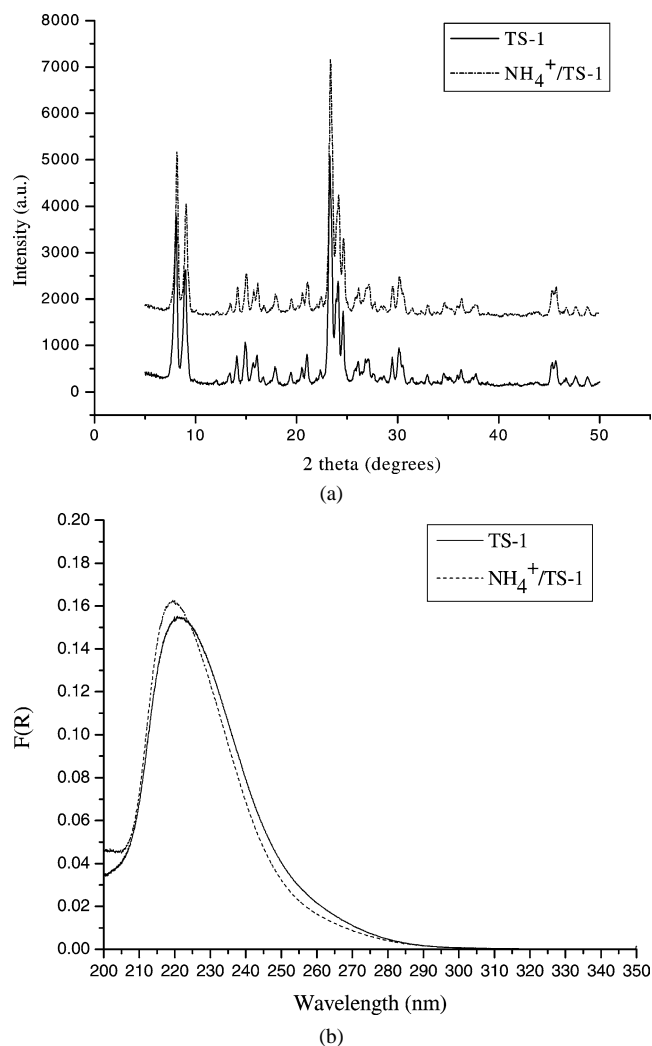


Fig. 2. (a) XRD patterns (a) and DRUV-vis spectra (b) of $\text{NH}_4^+/\text{TS-1}$ and TS-1 (same batch of TS-1).

The PO production rates reported (average rates) were measured after 4–6 h of steady-state activity at 200 °C. The average Au particle size for all of these catalysts was in the 5–6-nm range. This size range is slightly above the 2–5-nm range reported by Haruta and co-workers for the Au species that selectively forms PO. However, we did not observe a decrease in PO productivity due to the slightly larger average Au particle size. Furthermore, the number of observable Au particles is so small that it poses the question of whether gold less than 2 nm in size (and not visible in our TEM) could be responsible for at least a portion of the activity. The NH_4NO_3 -treated catalyst with a Au loading of 0.081 wt% (Fig. 1) had a rate of $134 \text{ g}_{\text{PO}} \text{ h}^{-1} \text{ kg}_{\text{cat}}^{-1}$ at 200 °C, whereas the best catalyst reported so far in the literature (by Haruta et al.) has a rate of $93 \text{ g}_{\text{PO}} \text{ h}^{-1} \text{ kg}_{\text{cat}}^{-1}$ at 160 °C [11]. Even though our current gas chromatograph does not enable us to directly measure the H_2 efficiency, with the use of the O_2 conversion, propylene conversion, and product selectivities, we have estimated a H_2 efficiency of $\sim 30\%$ (upper bound) for the above-mentioned catalyst that had a rate of $134 \text{ g}_{\text{PO}} \text{ h}^{-1} \text{ kg}_{\text{cat}}^{-1}$. Hydrogen efficiency was defined as the ratio of the hydrogen converted to make PO to the total amount of H_2 converted.

The trends in PO formation rates shown in Fig. 1 also indicate an optimal Au loading for these catalysts. We note specifically that, higher Au loadings (> 0.1 wt%), achieved with the NH_4NO_3 treatment for this support, were detrimental to catalyst stability. Catalysts with Au loadings less than 0.1 wt% maintained a constant PO productivity, even after 12 h of reaction at 200 °C, whereas catalysts with Au loadings of more than 0.1 wt% deactivated to about 80% of their original activity after the same period of time at 200 °C. Catalysts with Au loadings greater than 0.1 wt% have a higher number of Au particles compared with catalysts with lower Au loadings, and the increased proximity of sites could favor oligomerization of PO on the surface and thus lead to catalyst deactivation. Alternately, if the most active sites are highly dispersed Au clusters, the excess Au could overwhelm such sites and lead to deactivation. Subsequent experiments with different batches of TS-1 support materials

have indicated that the optimal Au loading is highly dependent on the particular support characteristics.

Table 1 contains a summary of Au loadings, Ti loadings, concentration of $\text{HAuCl}_4 \cdot x\text{H}_2\text{O}$ used, fraction of Au deposited, and PO productivity after steady-state kinetic analysis for NH_4NO_3 -treated and untreated Au/TS-1 catalysts made from different batches of TS-1 support materials. Samples with identical Ti loadings were prepared from the same batch of TS-1 support material. The results in Table 1 indicate that the NH_4NO_3 -pretreated support materials, on average, captured four times the Au content of catalysts prepared from the same batch of untreated TS-1 support materials and showed significantly higher rates. Compared with the results reported by Yap et al., where they observed 1–3% of the available Au in the solution being deposited on conventional TS-1 supports, NH_4NO_3 -treated TS-1 supports capture 4–70% of the available Au in the precursor solution under similar conditions. In terms of the activity enhancement due to the NH_4NO_3 pretreatment, we are particularly intrigued by the NH_4NO_3 -pretreated Au/TS-1 catalyst with a Au loading as low as 0.058 wt%, providing a 5% propylene conversion with 83% selectivity at 200 °C. This corresponds to a rate of $76 \text{ g}_{\text{PO}} \text{ h}^{-1} \text{ kg}_{\text{cat}}^{-1}$. This is a remarkably high rate for a catalyst with so little gold and implies a turnover frequency of over 0.1 molecule of PO per Au atom per second. It is also interesting to note that this catalyst regained its complete activity as the temperature cycle was repeated over a 40-h time period (Fig. 3).

The apparent activation energies for PO formation for catalysts NC_0.058_1.73 and C_0.015_1.73 (Table 1) were 30.3 kJ mol^{-1} and 32.4 kJ mol^{-1} , respectively. These values are comparable to the typical apparent activation energy (28.2 kJ mol^{-1}) for PO formation over Au/ TiO_2 catalysts (extracted from the data given in [1]). The range of values we typically obtain for Au/TS-1 catalysts is 25–35 kJ mol^{-1} . Catalysts NC_0.058_1.73 and C_0.015_1.73 were prepared from the same batch of TS-1 support material, where NC_0.058_1.73 was treated with NH_4NO_3 before Au deposition. The comparable apparent activation energies suggest that PO formation occurs via similar mechanisms for both NC_0.058_1.73 and C_0.015_1.73, and that the

Table 1
Comparison of NH_4NO_3 -treated and untreated Au/TS-1 catalysts prepared from different batches of TS-1 support materials

Catalyst ID	Au loading (wt%)	Ti loading (wt%)	Concentration of $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ (mg ml^{-1})	Fraction of Au deposited on support ^c (%)	PO rate ^b ($\text{g}_{\text{PO}} \text{ h}^{-1} \text{ kg}_{\text{cat}}^{-1}$)
NC_0.058_1.73 ^a	0.058	1.73	0.6	4.00	76
C_0.015_1.73	0.015	1.73	0.6	1.02	17
NC_0.058_2.06 ^a	0.058	2.06	0.6	4.12	41
C_0.015_2.06	0.015	2.06	0.6	1.08	7
NC_0.184_1.44 ^a	0.184	1.44	0.5	15.4	104
NC_5.0_2.20 ^a	5.000	2.20	3.0	69.7	60

The PO production rates (average rates) are reported after 4–6 h of steady state activity at 200 °C. Catalyst ID abbreviation: C_Au wt%_Ti wt%.

^a The letter “N” is indicative of NH_4NO_3 treated samples.

^b PO production rates (average rates) are reported after 4–6 h of steady-state activity at 200 °C and a space velocity of $7000 \text{ ml h}^{-1} \text{ g}_{\text{cat}}^{-1}$.

^c The percentage of Au deposited on support from the precursor solution $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ during DP ($100 \times (\text{mass of Au on dried catalyst}/\text{total mass of Au in precursor solution})$).

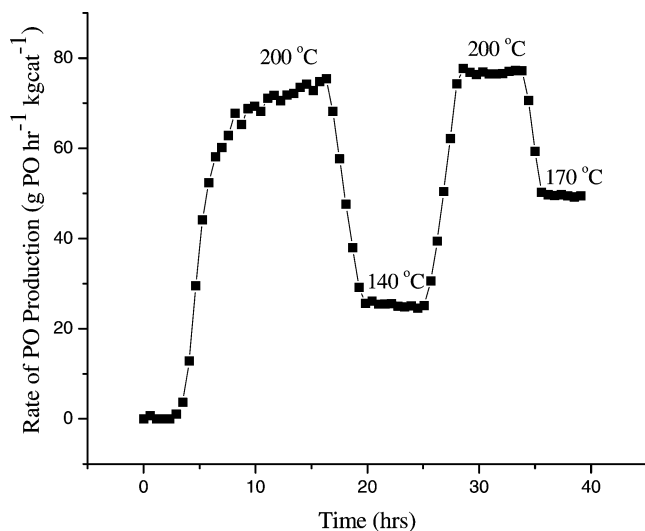


Fig. 3. Steady-state kinetic results for catalyst NC_0.058_1.73. This catalyst has an Au loading of 0.058 wt% with a 5% propylene conversion (83% selectivity) at 200 °C. The activity is completely regained on repeating the temperature cycle over a forty hour time period.

fourfold increase in rate can be attributed to an increase in the number of catalytically active Au sites caused by the NH_4NO_3 pretreatment.

Deposition precipitation with the typical concentration of $\text{HAuCl}_4 \cdot x\text{H}_2\text{O}$ solution used for untreated supports (3.0 mg ml^{-1}) resulted in Au loadings as high as 5.0 wt% for an NH_4NO_3 -treated Au/TS-1 catalyst, with an average Au particle size of $30.5 \pm 9.8 \text{ nm}$. Despite the large average Au particle size, this catalyst had an appreciable PO rate of $60 \text{ g PO h}^{-1} \text{ kg}_{\text{cat}}^{-1}$, with 75% selectivity for PO at 200 °C. However, significant deactivation (down to $40 \text{ g PO h}^{-1} \text{ kg}_{\text{cat}}^{-1}$) was observed for this catalyst as the temperature cycle was repeated. This clearly illustrates the enhancement in Au capture efficiency due to the NH_4NO_3 treatment and is consistent with our observations of high Au loadings causing catalyst deactivation with time on-stream [8].

To elucidate the role of NH_4NO_3 in the enhancement of activity, a few drops of 1 M NH_4NO_3 were added to a portion of *already synthesized* Au/TS-1 catalyst, which was then vacuum dried at room temperature before kinetic measurements. This catalyst did not show any enhancement in activity. In fact, the post-addition procedure caused the catalyst to rapidly deactivate, before even reaching the equivalent activity of the same batch of catalyst without the post-addition of NH_4NO_3 . This shows that, whereas NH_4NO_3 treatment before DP enhances activity, post-addition poisons the catalyst.

We have considered several probable mechanisms for the enhanced Au capture and activity in TS-1 due to the NH_4NO_3 pretreatment; these are discussed below. The preferential formation of an Au-ammine complex could result in an enhancement in the Au capture for NH_4NO_3 -treated TS-1 supports during DP. This Au-ammine complex could also account for the enhanced activity if it selectively deposits near Ti sites and consequently increases the proximity of Au to Ti. The higher PO formation rates per gram of Au (indicated

by the dotted lines in Fig. 1), for NH_4NO_3 -treated catalysts versus untreated catalysts, show a higher efficiency of creation of active sites, which could be associated with Au near Ti in these catalysts. Furthermore, the Au-ammine complex itself (or a decomposition product) could be a more active site for producing the electrophilic oxidant (H_2O_2) compared with Au species found in untreated Au/TS-1 catalysts. (Complex Au-ammines are reported to be stable at 190 °C, in liquid phase, in oxidizing environments [12].) Moreover, the enhancement in activity could be due to the removal of residual Cl^- ions (from the precursor HAuCl_4) by the NH_4^+ species during DP. Chlorine acts as a poison for Au catalysts by forming Au-Cl species. The mobility of this species on the surface may lead to sintering during activation [13] and thus to the formation of larger Au particles, which are inactive for PO formation.

In summary, we demonstrate a technique for increasing the Au capture efficiency of TS-1 supports. The NH_4NO_3 treatment significantly enhances the catalytically useful Au content and, hence, the activity of Au/TS-1 catalysts, as shown in Fig. 1. The NH_4NO_3 -treated catalyst with a very low Au loading (NC_0.058_1.73), but still showing significant activity, is further evidence for the enhancement in activity due to the NH_4NO_3 treatment. We have also shown that these catalysts have an optimal Au content that is dependent on the particular support characteristics. Further investigations intended to determine the nature of the nitrogen and gold species are under way.

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