

Direct Vapor Phase Propylene Epoxidation over Deposition-Precipitation Gold-Titania Catalysts in the Presence of H₂/O₂: Effects of Support, Neutralizing Agent, and Pretreatment[†]

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The effects of titanium connectivity, deposition solution neutralizing agent, and catalyst pretreatment were examined for a series of Au-on-titanium-containing supports for the direct gas-phase epoxidation of propylene using hydrogen and oxygen. The degree of titanium isolation was examined using pure titania, monolayer-titania on silica, submonolayer-titania on silica, and titanium silicalite-1 (TS-1) supports. Activity and selectivity were shown to increase as the degree of titanium isolation increased, with TS-1 and submonolayer-titania supports providing the best stability and yield. Isolation of the titanium was found to significantly reduce the cracking of propylene to ethanal and carbon dioxide. Sodium carbonate was found to be the best neutralizing agent for catalysts prepared using deposition–precipitation (DP). DP with ammonium hydroxide gave catalysts with reduced selectivity and activity. Titania-modified silica was found to produce better catalysts when the support was not calcined prior to gold deposition. Similarly, calcination was detrimental to catalysts prepared via deposition of a 2 nm gold colloid onto titania-modified supports even though the gold did not sinter. The beneficial effects of Ti site isolation and support acid/base control are best seen at higher temperatures, where only a few catalysts can maintain selectivity.

1. Introduction

Propylene oxide (PO) is a valuable chemical intermediate for the production of polyurethanes, polyethers, diols, and numerous other valuable chemical products ranging from propylene glycol in toothpaste and deodorants to the structural units of block copolymers. While ethylene is easily epoxidized heterogeneously over Ag/Al₂O₃, silver surfaces promote propylene combustion via attack of the acidic allylic hydrogen. In 1998, Haruta and co-workers discovered a highly selective route to propylene epoxidation over Au/TiO₂ using a combination of hydrogen and oxygen as the oxidants.¹ While generally considered to be inert, gold deposited onto titania was found to be capable of producing an electrophillic oxidant from hydrogen and oxygen that selectively adds oxygen across the double bond rather than attacking the weak bond of the allylic hydrogen.

In our first paper,² we demonstrated that there are five orders of magnitude in variation in activity based on observable gold surface area between various preparation methods. While essentially any method of combining titanium and gold resulted in some activity, the best activity by far was observed over catalysts prepared by deposition–precipitation (DP), a result that was previously asserted in the literature.^{1,3} Though not the goal at the time, the means used to combine gold and titanium resulted in substantial differences in the titanium phase. Catalysts prepared from leached AuTi₃ alloys are invariably different from those prepared from gold powder decorated with titanium or gold deposited on titania.

Information regarding the effect of the titanium phase on reactivity can be pieced together from several sources. However, a systematic examination of the effect of titanium connectivity has not yet been presented. In a series of papers by Haruta and co-workers, the proper gold-particle size, choice of titania support, and catalyst preparation method are shown to be crucial to both the PO activity and selectivity of Au/TiO₂ catalysts. Impregnation of HAuCl₄ onto any form of titania support resulted only in low activities to propane and CO₂.³ Chemical vapor deposition of gold via dimethyl-gold (III)-acetyl acetonate⁴ onto TS-1 yielded a material which produced mostly CO₂, with smaller amounts of propionaldehyde, acetone, and acetaldehyde.³ Gold deposited by deposition–precipitation, in all cases using Na₂CO₃, onto pure anatase or Ti–MCM-41 was over 95% selective to PO, but DP onto rutile was over 90% selective to CO₂.³ Gold deposited on amorphous TiO₂ bridged the activity and selectivity observed for rutile and anatase. DP of gold onto TS-1, TS-2, or Ti-β, while having > 90% PO selectivities at temperatures of 373 K, produced mostly propanal and CO₂ at temperatures in excess of 473 K.^{3,5} The production of propanal on all catalysts was attributed to the acid-catalyzed conversion of PO, and its formation was very dependent on catalyst washing. Titanosilicates that were thoroughly washed gave propanal, while the washing of other Au/TiO₂ catalysts resulted in high CO₂ formation due to the presence of residual contaminants Na⁺ and Cl[−].⁵ In subsequent work, using DP of gold onto Ti–MCM-41 and Ti–MCM-48, the MCM-48 materials were shown to be more active and selective than the Ti–MCM-41 materials, though both suffered from considerable deactivation after just a few hours on stream via the deposition of acidic and oligomeric species.⁶ Of all the catalysts tested, gold via DP on anatase, TiO₂-modified-SiO₂ or titanosilicates

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TABLE 1: Characterization Results for Catalyst Support Materials

support	abbreviation	TiO ₂ loading (wt%)	BET surface area (m ² /g)	micropore volume (cm ³ /g)	pore diameter (Å)
Cab-O-Sil M5	S	0	240	0	
degussa P25	P25	100	45	0	
anatase	A	100	8	0	
anatase	HSA	100	50	0	
rutile	R	100	1	0	
TiO ₂ -Modified SiO ₂ (α)	T-S(α)	15.1	220–240	0	
TiO ₂ -Modified SiO ₂ (β)	T-S(β)	21.0	220–240	0	
TiO ₂ -Modified SiO ₂ (γ)	T-S(γ)	13.6	220–240	0	
TiO ₂ -Modified SiO ₂ (δ)	T-S(δ)	8.6	220–240	0	
TiO ₂ -Modified SiO ₂ (ε)	T-S(ε)	1.3	220–240	0	
TiO ₂ -Modified SiO ₂ (ζ)	T-S(ζ)	0.8	220–240	0	
TS-1	TS1(49)	1.6	380–510	0.11	8.8

were considered most promising despite catalyst deactivation attributed to PO oligomerization.⁵ In a recent publication,⁷ Haruta and co-workers present a catalyst based on an amorphous titanasilicate consisting of a three-dimensional system of mesopores that not only produces industrially viable yields of PO but can also be easily regenerated in a mixture of hydrogen and oxygen.

The work of Nijhuis et al. using NH₄OH in a DP method to deposit gold onto anatase, a submonolayer TiO₂-modified-SiO₂, and TS-1 expanded upon the effect of titanium dispersion on catalyst deactivation.⁸ At temperatures below 393 K, PO selectivities were greater than 99%. While PO selectivity was high, maximum PO yields of greater than 2% could not be achieved due to product inhibition at high PO partial pressures. PO was lost via oligomerization on the Au/TiO₂ surface to molecules >C₆; the same type of dimerization that occurs on TiO₂ during aldol condensations of acetone. Attempts to improve the rate of propylene conversion to PO by raising the temperature from 393 K only resulted in combustion of the PO product. Batch experiments at varied reaction times confirmed that PO could react to further products on the Ti surface. The higher reactivity of DP TS-1 catalysts in their study was due to a suppression of further PO reactions because of the dispersed Ti phase. TS-1 maintained selectivity better than TiO₂-modified SiO₂, which, in turn, was better than DP on anatase. Thermogravimetric analysis showed that two types of carbon were deposited on Au/anatase catalysts. One was benign, while the other was associated with deactivation. Au/TS-1 catalysts only contained benign carbon. A subsequent FTIR study on Au/TiO₂/SiO₂ found that PO and mixtures of oxygen, hydrogen, and propylene yielded the same bidentate propoxy group formed over adjacent titanium sites, implying this species causes deactivation on surfaces containing extended titania phases.⁹ The activity of catalysts with highly dispersed titanium was not affected by the formation of the propoxy group, implying its formation on sites different than those responsible for epoxidation. Evidence of oligomerization and dimerization were not found. However, the study was carried out at pressures much less than atmospheric. As for the nature of the gold on TiO₂, XPS and Mössbauer spectroscopy showed only metallic gold contributions to catalytic activity.¹⁰

A set of DP catalysts, prepared here using CsOH, NH₄OH, and Na₂CO₃ as neutralizing agents, was created to further examine the role TiO₂ plays in propylene epoxidation. The effects of catalyst pretreatment on the activity of the catalyst are also examined. This paper extends the work of Haruta et al. and Moulijn et al. on the type of support necessary, focusing specifically the effect of titanium connectivity on catalyst performance, as well as other preparatory factors that lead to active propylene epoxidation catalysts that sustain selectivity at 473 K.

2. Catalytic Materials

2.1. Support Preparation and Characterization. The supports examined in this work include Cab-O-Sil M5 SiO₂ (Cabot Corporation, 99.95%), TiO₂ P25 (Degussa, > 97%), anatase in two forms, A (Aldrich, 99.9+%) and HSA (Alfa Aesar, 99.9%), and rutile powder (Aldrich, 99.99%), all of which were utilized as delivered.

TiO₂-modified SiO₂ supports were prepared by impregnation, to typically 15 wt% TiO₂, of the M5 SiO₂ support with titanium (IV) isopropoxide (TTIP, Aldrich Chemicals, 97.0) in pentane. The solution was stirred until the pentane evaporated. For supports where less than a monolayer of TiO₂ was added, usually around 1 wt% TiO₂, the appropriate amount of TTIP was added to M5 in 2-propanol while stirring. Agitation was continued for about 2 h, after which the isopropanol was removed by rotary evaporation under vacuum. The resulting solid was either utilized as synthesized or calcined at 773 K prior to gold deposition. The TiO₂-modified SiO₂ supports had a BET surface area of nearly 220 m²/g, which is very close to the original surface area of the M5 (200–260 m²/g). Metal loadings were determined using a Perkin-Elmer 3110 atomic adsorption (AA) spectrometer, while surface area measurements were obtained from dinitrogen isotherms using a Micromeritics ASAP 2000. Titanium silicalite-1 was synthesized according to the original patent by Taramasso et al.¹¹

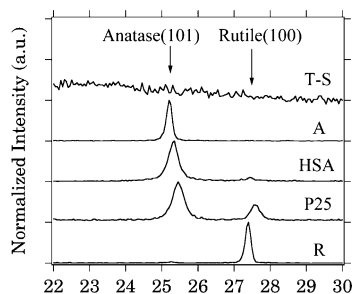
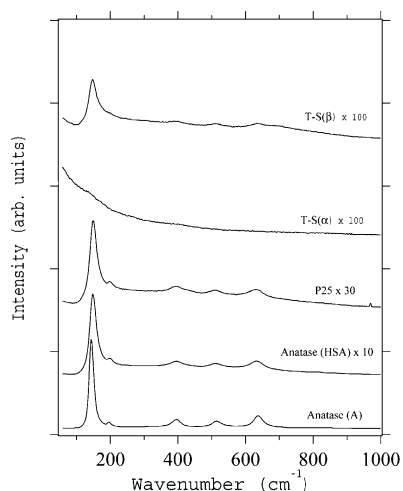
A summary of the characterization results for the different support materials is given in Table 1. Included is the abbreviation by which each support is referred. X-ray photoelectron spectroscopy (XPS) was performed using a Perkin-Elmer 5300 Series spectrometer outfitted with a hemispherical detector, Raman spectra were obtained using a Laser Diode spectrometer employing a 300 mW beam at 785 nm, and transmission electron micrographs were obtained using a JEOL 2000 FX microscope operating at 200 keV.

Powder X-ray Diffraction (XRD) was performed on all catalyst supports to determine the volume-averaged crystallographic phases present using a Siemens D500 Diffractometer employing Cu Kα radiation. The XRD patterns in Figure 1 show the Aldrich anatase (A) and rutile (R) to be pure, the P25 to be a mixture of a significant rutile phase with the majority anatase, and the M5 to be amorphous. The Alfa Aesar anatase contained only a small amount of rutile. Since XRD is a volume-averaged technique and the phase transformation from anatase to rutile is complex,¹² the ratio of anatase to rutile on the P25 surface is not necessarily known from these data. The TiO₂-modified SiO₂ samples remained amorphous after deposition of TTIP on silica since no large crystalline TiO₂ domains were observed.

Raman spectroscopy of some selected catalyst supports was performed as a further verification of support-phase crystallinity, with the results presented in Figure 2. For the A, HSA, and

TABLE 2: Characterization Results for Various Deposition–Precipitation and Colloidal Catalysts

catalyst	preparation method	gold loading (wt %)	D_p (nm)	charge wt (g)
Au(DP)/P25	Au DP on P25	1.1	7.4 ± 2.3	0.12
Au(DP)/A	Au DP on Aldrich anatase	0.2	4.5 ± 1.0	0.11
Au(DP)/HSA	Au DP on Aesar anatase	0.6	4.5 ± 1.0	0.06
Au(DP)/T-S(α)	Au DP with Na_2CO_3 on modified-M5	0.5	4.2 ± 1.0	0.12
Au(DP)/T-S(β)	Au DP with Na_2CO_3 on modified-M5	1.1	5.4 ± 1.5	0.05
Au(DP)/T-S(γ)	Au DP with CsOH on modified-M5	1.3	7.5 ± 1.4	0.10
Au(DP)/T-S(δ)	Au DP with NH_4OH on modified-M5	2.7	8.3 ± 2.8	0.07
Au(DP)/cT-S(ϵ)	Au DP with Na_2CO_3 on calcined T-S(ϵ)	0.2	10.5 ± 4.0	0.28
Au(DP)/uT-S(ϵ)	Au DP with Na_2CO_3 on uncalcined T-S(ϵ)	1.0	6.0 ± 2.6	0.22
cAu(C)/T-S(ζ)	Gold 2 nm colloid on T-S(ζ), calcined	0.02	2.4 ± 1.1^a	0.32
uAu(C)/T-S(ζ)	Gold 2 nm colloid on T-S(ζ), uncalcined	0.02	2.4 ± 1.1^a	0.32
Au(DP)/TS1(49)	Au DP with Na_2CO_3 on TS1(49)	0.5	5.5 ± 2.6	0.21

^a Size distribution of the colloid as received.**Figure 1.** X-ray diffraction powder pattern of representative support materials.**Figure 2.** Raman characterization of select TiO_2 supports.

P25 supports, the clear lines at 145, 396, 515, and 638 cm^{-1} are proof of the anatase crystalline structure.¹³ For the P25 support, there may be indications of the rutile crystalline structure with broad shoulders at 600 and 450 cm^{-1} underneath the stronger anatase lines, but curve fitting was not performed to verify their presence. The T-S(α) support does not show any signs of crystallinity while T-S(β) does show some anatase phase, probably a result of TiO_2 loading in excess of the 15 wt% that is considered the upper loading for a monolayer on SiO_2 of this type.¹⁴ Raman spectroscopy performed on the TS-1 samples (not shown), showed only a broad line at 400 cm^{-1} , indicative of the MFI structure; however, a peak at 960 cm^{-1} , indicative of Ti lattice substitution, was not observed.¹⁵ It is possible that the acquisition time for the zeolite samples was not long enough to observe this relatively weak feature. The absence of a Raman absorption band for anatase at 144 cm^{-1} combined with an XRD pattern matching that of the orthorhombic MFI structure show that TS-1 of reasonable quality was synthesized.

2.2. Gold Deposition and Characterization. A majority of catalysts were prepared via DP resulting from the neutralization to pH 7–9 of a room-temperature, aqueous HAuCl_4 solution containing the desired TiO_2 support. Two additional catalysts were made by deposition of colloidal gold. A complete list of these catalysts can be found in Table 2. Some of the results over these catalysts have been previously discussed.²

The DP procedure used was similar to that of ref 15. In most cases, Na_2CO_3 was used as the neutralizing agent, but one catalyst each was prepared using CsOH and NH_4OH . The suspensions were stirred vigorously for 3–4 h in the neutralizing solution before being filtered and washed $3 \times$ in 100 mL. Most catalysts were dried overnight in vacuo at 393 K and then calcined at 673 K unless otherwise specified. Gold loading was determined by atomic absorption.

For comparison purposes, two catalysts, Au(C)/T-S(ζ) and Au(C)/uT-S(ζ), were prepared by dispersing a 2 nm gold colloid, stabilized by citrate ions (Vector Laboratories, Inc.) on a 0.8 wt% T-S support prepared in 2-propanol as described previously. Experience indicates that small, atomic-scale gold clusters are also present in colloids prepared by the gold reduction techniques used in the preparation of commercial gold colloids.¹⁷ The TEM micrograph of this cluster sol is shown in Figure 3. Gold particles could not be clearly defined on the surface in TEM of the Au(C) catalysts before or after reaction, suggesting that the gold remains well dispersed under reaction conditions on both samples.

Figure 4 shows a TEM micrograph of a DP catalyst prepared on TS-1, labeled Au(DP)TS1(49). Figure 5 shows that, for a catalyst prepared on an uncalcined support, Au(DP)/uT-S(ϵ), the morphology of the resultant gold particles appears very similar to that of gold particles on a catalyst produced by coprecipitation of gold and titanium whose activity has been previously described.² The appearance of the gold particles on the calcined support cT-S(ϵ), as well as T-S(β), T-S(γ), and T-S(δ), is very similar to that of the gold particles on T-S(α) in Figure 1 of ref 2.

Steady-state kinetics were obtained for each catalyst using a $1/2$ -inch stainless steel tubular reactor operating in the differential conversion regime. The temperature of the catalyst bed was monitored with a type-K thermocouple. Gases were supplied at 35 sccm at a composition of 10/10/10/70 volume % propylene (99.9%), oxygen (99.9995%), hydrogen (99.9995%), and helium (99.9995%). Effluent from the reactor was analyzed by a Varian 3740 gas chromatograph. Hydrogen, oxygen, methane, carbon dioxide, propylene, and propane were separated using a $1/8\text{ in.} \times 8\text{ ft}$ Chromosorb 102 packed column (Supelco, Inc.) and detected using a thermal conductivity detector. Partial oxidation products (ethanal, propylene oxide, propanal, acetone, and acrolein) were separated via a $0.53\text{ mm} \times 60\text{ m}$ Supelcowax

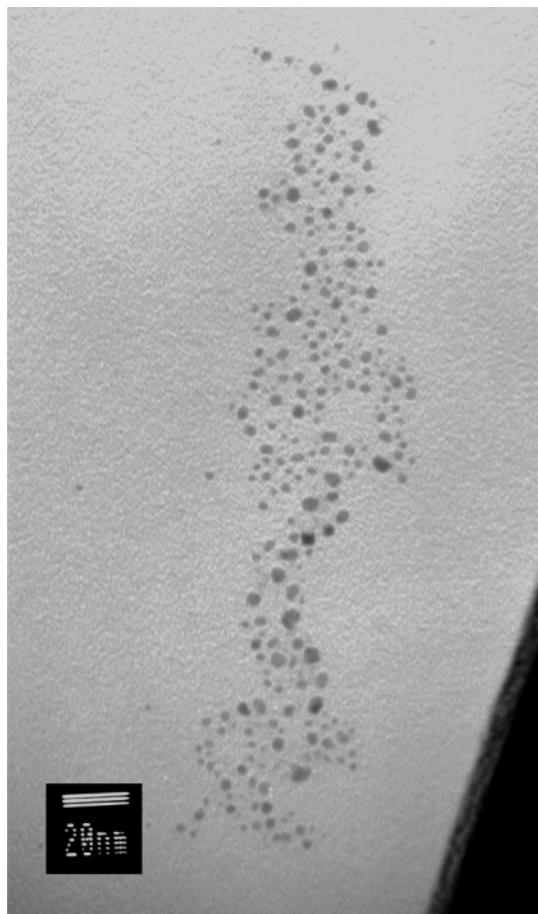


Figure 3. Transmission electron micrograph of the cluster sol used in the preparation of Au(C)/T-S(ζ).

10 capillary column (Supelco, Inc.) and detected using a flame ionization detector. Due to the nonlinear response of hydrogen when using helium as a carrier gas, the selectivity of hydrogen was not quantified.

Normalized reaction rates were converted to turnover frequencies (TOF) by assuming that every gold surface atom is active for epoxidation. The dispersion of each catalyst was calculated using the average gold particle diameter ($\langle D_p \rangle$) and assuming uniform hemispherical particles. This recasting of the rate did not significantly alter the relative values of the examined catalysts since the dispersion and metal loadings were roughly of the same order of magnitude for all catalysts.

3. Activity Results

The effects of titanium connectivity, neutralizing agent, and catalyst pretreatment were examined using a series of catalysts prepared by DP of gold and deposition of a gold colloid on supports ranging from crystalline titanias to titanium dispersed in/on silica matrixes.

3.1. TiO₂ Phase Effects. The series of support materials used in this study, Degussa P25, anatase (A), a high surface area anatase (HSA), monolayer (T-S(α)) and submonolayer (T-S(ϵ)) TiO₂-modified SiO₂, and TS-1 (TS1(49), Si/Ti = 49) represents an increasing level of isolation of titanium. The PO activity for all the aforementioned catalysts and product selectivities for the P25, A, HAS, and T-S(α) catalysts can be found in Figures 6 and 7, respectively. The activity and selectivity results reported here for both the Au(DP)/T-S(α) and the Au(DP)/P25 material are very similar for those reported by Nijhuis et al. when compared at 373 K.⁸ The remaining catalysts with the submono-

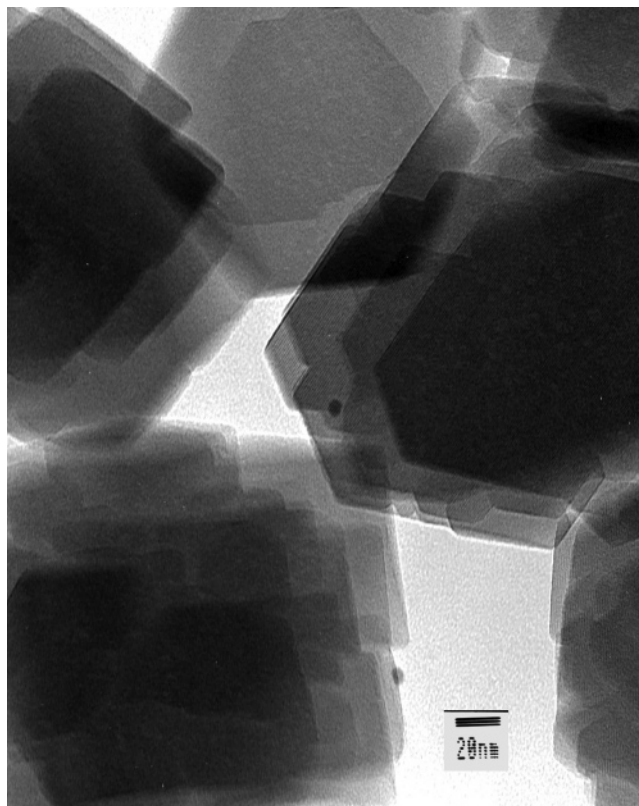


Figure 4. Transmission electron micrograph of catalyst Au(DP)/TS1-(49).

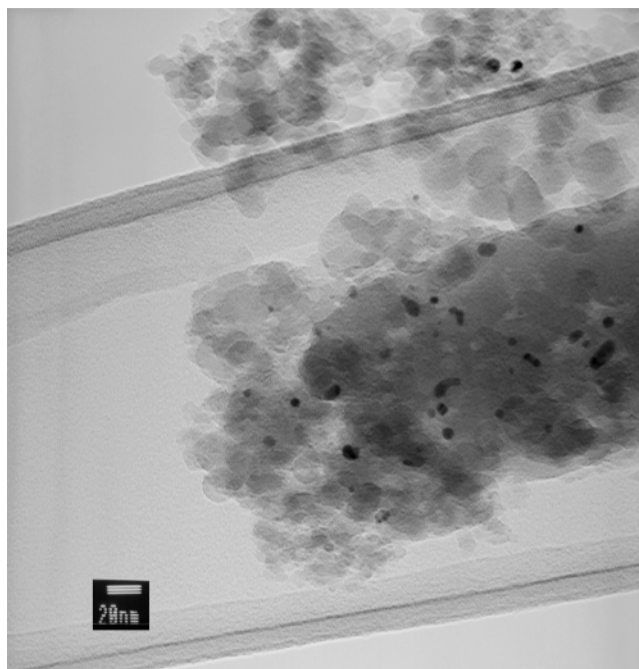


Figure 5. Transmission electron micrograph of catalyst Au(DP)/uT-S(ϵ).

layer Ti supports, including TS1(49), have their product selectivities shown in Figure 8.

The effect of the TiO₂ phase on PO activity as seen from Figure 6 is dramatic and is found to correlate with TiO₂ connectivity, such that activity decreases with increasing titanium connectivity. While many catalysts in this section have a similar TOF at 373 K, four orders of magnitude variation in TOF is seen as the temperature reaches 473 K. A DP catalyst

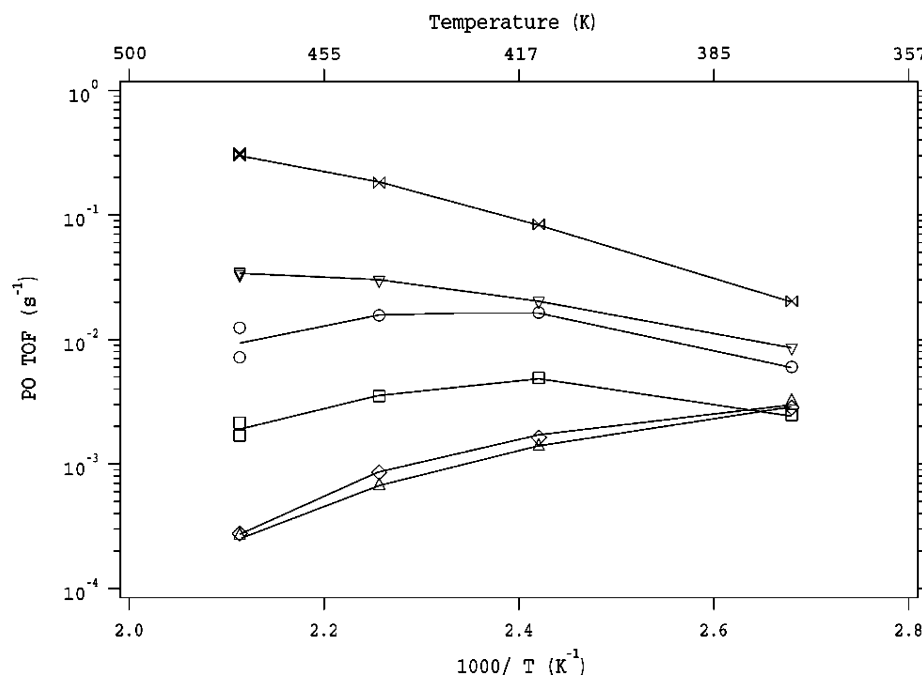


Figure 6. Effect of TiO_2 support phase on PO activity over deposition-precipitation catalysts. TOF: (Δ) Au(DP)/P25, (\Diamond) Au(DP)/HSA, (\square) Au(DP)/A, (\circ) Au(DP)/T-S(α), (∇) Au(DP)/uT-S(ϵ), (\times) Au(DP)/TS1(49).

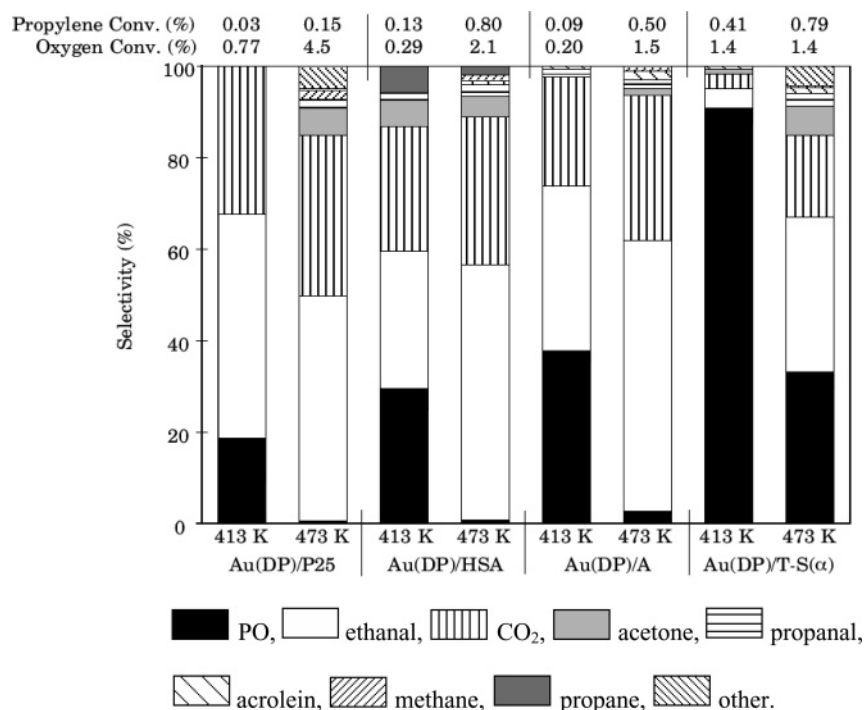


Figure 7. PO selectivity over selected deposition-precipitation catalysts.

prepared on a low-surface-area rutile ($1 \text{ m}^2/\text{g}$) had very few Au particles and had no activity. The rutile, despite the low surface area, adequately represents a titania phase with the highest degree of connectivity, i.e., the highest titanium density per unit area. The Au(DP)/P25 catalysts had very low PO activity and selectivity, while a slight improvement was made, mostly at lower temperatures, by going to a similar high-surface support, Au(DP)/HSA, that contained significantly less rutile phase. The Au(DP)/A catalyst was the best of the three catalysts containing anatase phases, showing better maintained PO selectivity, including one $>80\%$ at 373 K . The T-S(α) support provided the next best catalyst. Further increasing the TiO_2

dispersion by producing a submonolayer TiO_2 catalyst, Au(DP)/uT-S(ϵ), resulted in continued improvement in both sustained PO activity and selectivity. This catalyst was also used to demonstrate the effect of residence time on PO selectivity. The flow rate of reactants was increased to 100 sccm . This resulted (Figure 8) in the expected decrease in conversion with a significant increase in selectivity, showing that PO can be consumed at lower WHSV (weight hourly space velocity). The catalyst prepared on TS-1 had the highest PO activity and selectivity at all temperatures. The TiO_2 -based supports for propylene epoxidation can be ranked as: rutile $<$ anatase $<$ monolayer T-S $<$ submonolayer T-S $<$ TS-1.

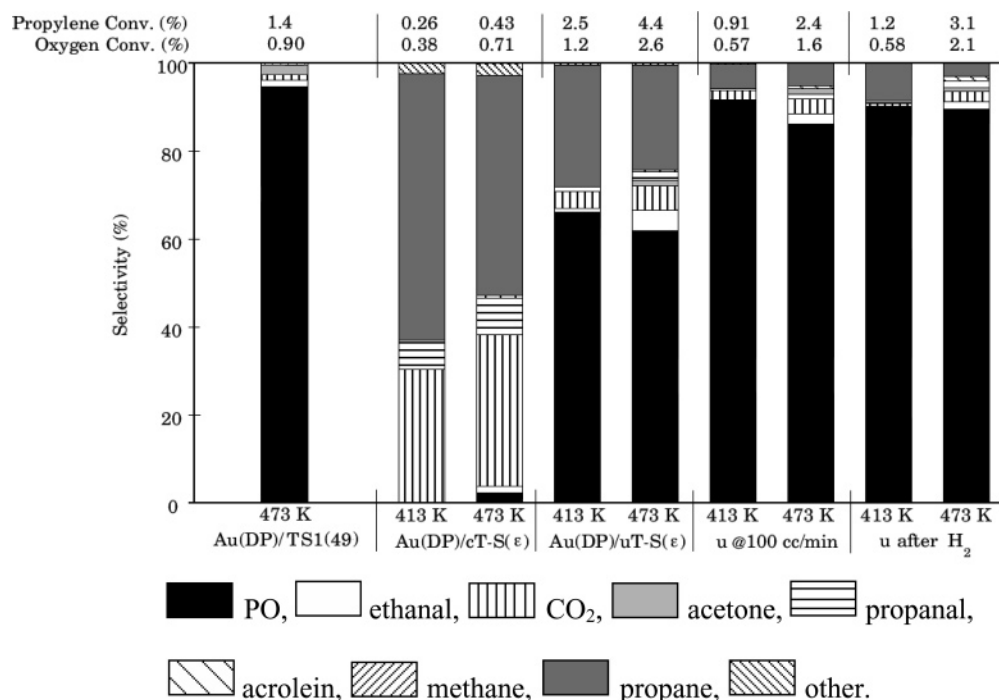


Figure 8. PO Selectivity over selected deposition–precipitation catalysts prepared on calcined and uncalcined submonolayer Ti supports and TS-1. Also presented is the selectivity for the uncalcined support at 100 sccm total flow rate and following treatments in O₂ and H₂ at 473 K.

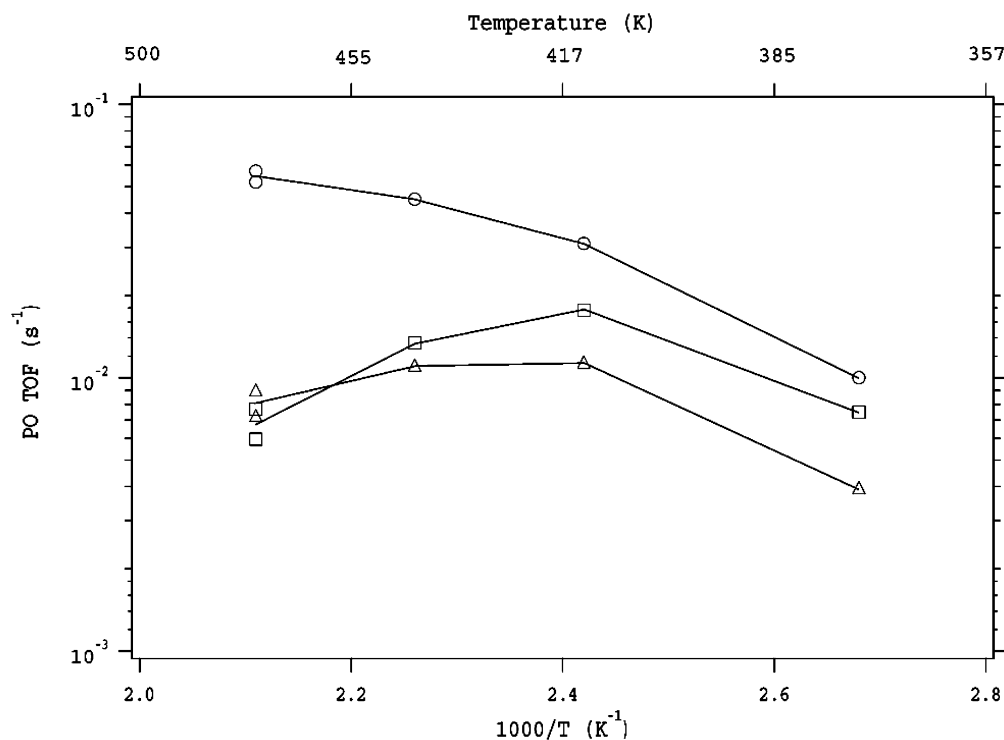


Figure 9. Effect of neutralizing agent on PO activity over deposition-precipitation catalysts. TOF: (Δ) Au(DP)/T-S(γ) using CsOH, (□) Au(DP)/T-S(δ) using NH₄OH, (○) Au(DP)/T-S(β) using Na₂CO₃.

It is interesting to note the dramatic effect that small changes in the titania phase have on the overall PO activity and selectivity both here and in the work of Haruta et al.³

3.2. Neutralizing Agent Effects. Any number of neutralizing agents can be employed in the DP of gold. The effect of neutralizing agent on the epoxidation of propylene was examined on three different T-S supports on which gold was deposited using Na₂CO₃ (Au(DP)/T-S(β)), CsOH (Au(DP)/T-S(γ)), and NH₄OH (Au(DP)/T-S(δ)) as neutralizing agents. The activity

and selectivity for these catalysts are shown in Figures 9 and 10, respectively.

Different neutralizing agents have some effect on ultimate catalyst performance, although not to the degree of TiO₂ support morphology. The catalysts prepared by the ammonium and cesium hydroxides have slightly lower activity than those prepared by Na₂CO₃, especially at 473 K. The differences at that temperature are magnified in the product selectivities of these catalysts in Figure 10. Catalyst T-S(β) has the highest

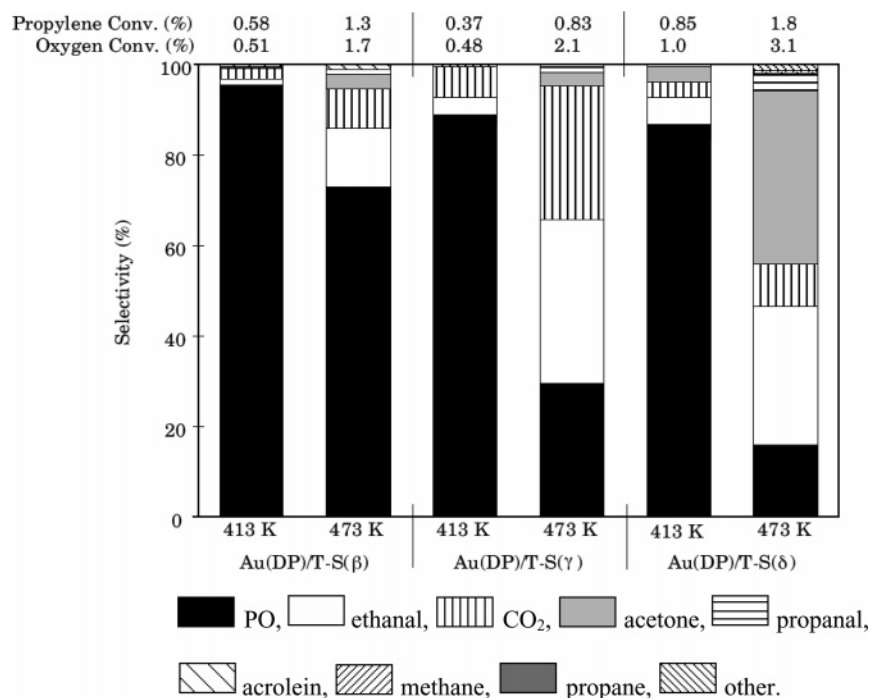


Figure 10. Effect of neutralizing agent on PO selectivity over deposition–precipitation catalysts.

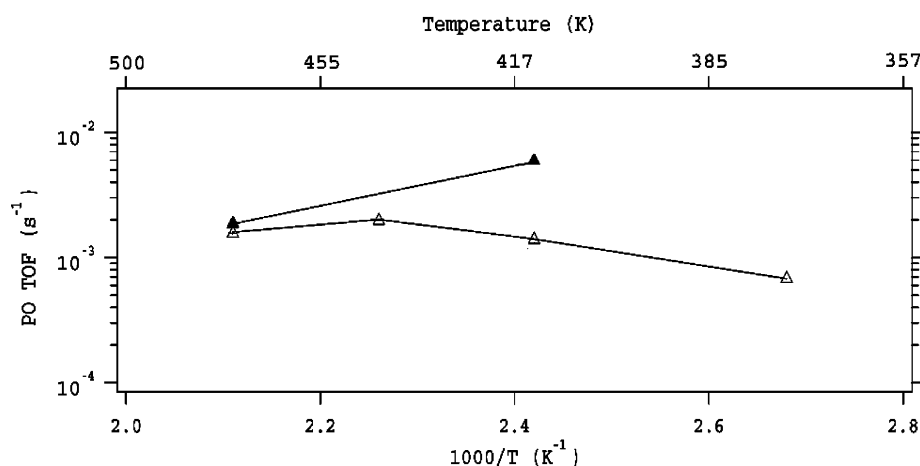


Figure 11. PO activity over colloidal Au(C)/T-S(ζ) with different pretreatments. TOF: (Δ) cAu(C)/T-S(ζ), (▲) uAu(C)/T-S(ζ).

PO selectivity, while T-S(γ) is slightly worse. The lowest PO selectivity is for the catalyst prepared with NH₄OH (T-S(δ)), which has much higher selectivity to acetone than all other DP catalysts used in this study.

3.3. Effects of Pretreatment on Epoxidation Activity. The activity of Au(DP)/uT-S(ε) was described previously in section 3.1. A very different catalyst was created, Au(DP)/cT-S(ε), when the T-S(ε) support was calcined prior to deposition. Figure 8 shows that a much larger propylene conversion, with relatively high selectivity to PO, was observed over the uncalcined support, while combustion products and propane dominated products of the support calcined prior to gold deposition. The order of magnitude higher propylene conversion over the uncalcined support might be partially explained by the ability of the catalyst on this uncalcined support to produce gold particles with a smaller $\langle D_p \rangle$ during the DP procedure (see Table 2), but this does not explain the observed selectivity differences. The potential effects of oxidation and reduction treatments were examined at 473 K and resulted in roughly a 25% decrease in conversion and a 25% increase in selectivity, as shown in Figure 8.

In another set of catalysts, commercially available citrate stabilized gold colloid with particles nominally 2 nm in diameter were deposited on a submonolayer TiO₂-modified SiO₂ support that was left uncalcined in an attempt to make the surface more adhesive to the charged colloidal particles. This catalyst was separated into two batches, one of which was calcined, cAu(C)/T-S(ζ), and the other, uAu(C)/T-S(ζ), used as prepared. The catalytic activity for each of these catalysts can be found in Figure 11, while the selectivities, compared at 443 and 473 K, can be found in Figure 12. TEM analysis did not reveal discernible gold particles, therefore, the catalyst TOF was calculated assuming that the average particle size on the catalyst was the same as that for the original colloid shown in Figure 3. The temperature program for the two catalysts was slightly different. While the calcined sample was run through a four-stage, staggered, high-to-low-temperature program (473–413–443–373K), the uncalcined sample, uAu(C)/T-S(ζ), was subjected to a temperature program that was roughly the opposite (373–443–413–473K). The uAu(C)/T-S(ζ) catalyst did not become active until the program reached 473 K, presumably where the citrate encapsulant could be removed, allowing access

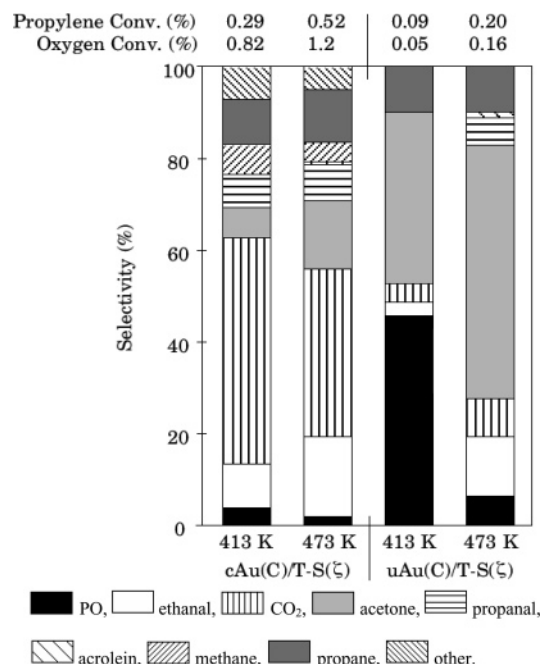


Figure 12. PO selectivity over colloidal Au(C)/T-S(ζ).

to a gold–titania interface. For this reason, uAu(C)/T-S(ζ) was retested at 443 K for comparison to cAu(C)/T-S(ζ). Reanalysis at 413 K was not performed.

The resultant catalysts, while tested with equivalent reactor charges, exhibited remarkably different activities and product distributions. The uncalcined catalyst, uAu(C)/T-S(ζ), was almost 50% selective to PO at 443 K as compared to a much lower value on the calcined sample. While the total selectivity to partial oxygenates over both materials was roughly equivalent for the same catalyst charge, the uncalcined sample was much more active for oxygenate formation, producing much smaller amounts of combustion products as compared to cAu(C)/T-S(ζ). Large amounts of acetone were observed over uAu(C)/T-S(ζ) and, as will be discussed in the next section, this is indicative of PO formation. It should not be overlooked that the performance of the uncalcined catalyst, uAu(C)/T-S(ζ), may have been due to on-stream activation at 473 K, resulting in active sites that were somehow irreversibly quenched or destroyed during the calcination. In any case, the considerable differences in activity demonstrate a remarkable ability of the catalyst pretreatment before reaction to control both the number and type of active sites on the catalyst.

4. Discussion

Even within a subset of the most active preparation methods such as DP, not all catalytic supports produce equivalent activity. Figure 6 clearly shows that PO activity varies on the basis of the support used and that the activity increases with a decrease in the TiO₂ connectivity. While these catalysts represent a range of gold loadings in addition to variations in support material, the resultant gold particle sizes are within the standard deviations of the particle-size distribution. This, combined with the normalization of the rate to the total surface gold atoms, results in data indicative of changes only in the titanium connectivity. TS-1 represents the ultimate in TiO₂ dispersion, forcing TiO₂ into crystallographically defined isolation within a zeolitic SiO₂ matrix, providing an even greater lack of connectivity and better support than the submonolayer titanium-modified silicas for the epoxidation of propylene. The appearance of either anatase or

rutile phases results in decreased PO activity and selectivity relative to more disordered/isolated TiO₂. Deposition of gold onto a low-surface-area pure rutile support does not show any PO activity, while a decrease of PO activity was observed with an increase in the characteristic rutile XRD line at $2\theta = 28^\circ$ for catalysts Au(DP)/HSA and Au(DP)/P25. The variation of PO activity with DP methods on different supports has also been reported by Haruta and co-workers.³

As gold is deposited onto a properly disordered TiO₂ phase on TiO₂-modified SiO₂ catalysts, there is an additional effect of both the neutralizing agent used in the DP method and the hydration state of the TiO₂ phase before gold deposition. While the three supports used in this series are not identical, each contains a molar excess of titanium relative to gold such that each gold atom has a titanium site on which to anchor. When gold particles rather than individual atoms are considered to be the source of activity, the surface titanium species are in even greater excess. As a result, changes in activity or selectivity of these catalysts can be attributed to changes in the neutralizing agent. In addition, the small anatase impurity of T-S(β) would only serve to decrease the activity and selectivity, resulting in an under-representation of the effect Na₂CO₃ has during DP. Figures 9 and 10 show that similarly prepared DP catalysts on monolayer TiO₂-modified SiO₂ supports prepared with Na₂CO₃, CsOH, or NH₄OH do not have equivalent PO activities and selectivities. Small variations in the local TiO₂ phase structure as mentioned previously aside, the catalyst prepared with NH₄OH, Au(DP)/T-S(δ), shows much more acetone with slightly decreased ethanal and CO₂ formation as compared to DP catalysts prepared with Na₂CO₃ or CsOH. In support of this result are the DP catalysts prepared with NH₄OH of Nijhuis et al.,⁸ which, while showing similar activity and selectivity at 373 K to those in this work, have lower PO selectivity at high temperatures. Our XPS analysis confirms that Na⁺ or Cs⁺ is deposited on the catalyst surface during DP and remains after calcinations and reaction, while catalysts prepared with NH₄⁺ are left without a surface alkali counterion. The literature shows that alkali may block Lewis acid/base pairs on TiO₂¹⁸ or alter the reactivity of the TiO₂ surface.¹⁹ The introduction of the NH₄⁺ onto the catalyst's surface and the resultant increase in selectivity to acetone implies that the basic nature of the support has increased, resulting in a ring-opening of the epoxide to the ketone.

XPS has also detected large amounts of K present in the Aldrich anatase, A, used in this work, while the Alfa anatase, HSA, has little or no Na or K as delivered. This, in conjunction with the minor amount of rutile present in HSA, may account for the drastic differences in activity between Au(DP)/A and Au(DP)/HSA, as observed in Figure 6. P25 is known to have stronger acid/base character than normal anatase²⁰ and may further affect final reactivity if not properly neutralized with sufficient alkali. The conclusion is that the presence of surface alkali has a positive effect on PO activity and selectivity, presumably by blocking further PO reactions. It is not clear from this study if one type of alkali is better than another, or if alkali is involved in the reduced formation of ethanal and CO₂, which is the major loss of selectivity over these materials at higher temperatures.² While the benefits of promotion with CsCl on the hydrogen efficiency of these catalysts have been reported,²¹ the level of Cs⁺ detected on our catalyst via XPS was below the high levels needed for this effect.

As discussed above, calcinations of TiO₂ before gold deposition have a considerable effect on PO activity. As shown in Figure 8, a comparison between the propylene oxidation results

over two catalysts prepared from the same support, T-S(ϵ), in which one of the supports was calcined prior to DP of gold (Au(DP)/cT-S(ϵ)) and the other was not calcined (Au(DP)/uT-S(ϵ)) shows that the catalyst on the uncalcined support produced significantly more PO. Au(DP)/cT-S(ϵ) has almost no PO activity, producing mostly propane or combustion products. In addition, Table 2 shows that while the Au loading of the uncalcined material is higher, its average particle size, $\langle D_p \rangle$, is lower. One might expect that since Au(DP)/uT-S(ϵ) has the smaller $\langle D_p \rangle$, it might be more likely to have more of the <2 nm particles that show hydrogenation activity under these conditions¹ than Au(DP)/cT-S(ϵ) with a larger $\langle D_p \rangle$. This is not what is observed. While the $\langle D_p \rangle$ reported here does not directly represent the possible presence of 2 nm particles on the catalyst surface, these differences in observed activity must either be attributed to the small Au particles that cannot be seen or to a subtle change in Au morphology and/or Au–Ti perimeter-site chemistry of the particles that are visible. The higher loading of the uncalcined support as compared to cT-S(ϵ) definitely suggests that hydrated gold species interact more strongly with an uncalcined surface, which is likely to be in a higher state of hydration prior to calcination. The state of TiO₂ hydration may be very important in the formation of the active epoxidation site and in determining whether gold species with hydrogenation or epoxidation activity are generated. The potential effect of oxidation/reduction cycles on these catalysts was examined using a mild treatment of Au(DP)/uT-S(ϵ) in O₂/H₂ at 473 K. The result was a reduction in the propane activity and an increase in selectivity to PO, without drastically affecting the overall PO TOF. This is consistent with sintering of 1–2 nm propane producing particles, but the reason the PO activity remained unaffected is unclear. It may be that the gold species producing PO is unaffected by this treatment, while the sintering of a separate gold species accounts for the propane activity loss.

Post-calcination of the catalyst after gold deposition also can have dramatic effects on catalyst activity and product distribution. Calcinations of Au(C)/T-S(ζ) resulted in a much more active propylene conversion catalyst but a much less PO-selective material. Large amounts of CO₂ and ethanal are seen with cAu(C)/T-S(ζ) relative to the uncalcined material, uAu(C)/T-S(ζ). The lower activity of uAu(C)/T-S(ζ) may be partially attributed to its evaluation by low-to-high temperature program, which may not have removed all of the citrate stabilizer until a temperature of 473 K was reached, but this does not explain the large selectivity variation. The increased selectivity to acetone also implies the basic ring-opening of PO, potentially as a result of citrate remaining on the surface. Ultimately the calcinations of cAu(C)/T-S(ζ) must have caused migration of TiO₂ and/or Au, resulting in a nonbeneficial Au–Ti contact synergy. Gold species have previously been shown to promote TiO₂ support modification during heat treatments.²² Interestingly, despite the colloid used to prepare these catalysts having a mean particle size near 2 nm, very little propane is produced. One would expect more propane from the uncalcined sample brought up to temperature online at a slow rate, which should reduce the opportunity for particle sintering. This was not the observation. Clearly, calcinations can result in less PO-productive catalysts for certain preparations, perhaps by activating PO destruction sites (as in the case of high acetone selectivity) or eliminating PO production sites.

Many authors have noted the drastic effects of calcinations on the activity of Au/TiO₂ catalysts for low-temperature CO oxidation.^{23,24,25} It has been shown that for initially less optimally contacted Au/TiO₂ catalysts, such as those prepared from

colloids or impregnation, activity can be improved with increasing calcination temperatures up to 873 K^{23,24} or with higher-temperature reduction–oxidation cycles.^{25,26} Tsubota et al. have ascribed increased CO oxidation activity for TiO₂-supported gold colloids calcined at higher temperatures to the formation of stronger interactions between the gold and titania phases.²⁴ This work, however, shows that these gold/titania interactions must be detrimental to PO activity and that catalysts synthesized from colloidal gold catalysts are best used uncalcined (as was previously indicated by refs 27 and 28). Catalysts that initially had much higher activities than those prepared from colloids, such as DP catalysts, showed optimal calcinations temperatures of about 673 K, above which activity is seen to decrease.^{23,24} In this work, mild temperature treatment of Au(DP)/P25 (results not shown) resulted in an increase in PO activity and selectivity, despite sintering and decreased propylene conversion. This is most likely due to an increased number of Au–Ti bonds, perhaps through a synergy similar to an SMSI state, although such a state appears to have been discounted for impregnated catalysts.¹ Although all of the catalysts used in this work were calcined following gold deposition, some literature claims that this calcination step is not required and that as-deposited hydrated gold-surface species are more active.^{28,29,30,31}

The local structure of the TiO₂ phase near the active gold site is an extremely important factor in determining the resultant activity of a Au/TiO₂ catalyst. The present study suggests a strong PO–support interaction in which the presence of Ti–O–Ti bonds seems to be very detrimental to PO selectivity. Isolated TiO₂ moieties serve to control carbon deposition from PO oligomerization, which results in substantial catalyst deactivation at temperatures near 373 K.^{21,8} Our results show that this carbon film is not static, and at temperatures near 473 K, catalyst deactivation is slowed, owing to decreased deposition or partial removal of the deposited carbon. The higher the temperature at which one can maintain PO selectivity, the less the problem PO oligomerization should pose at steady state. Regardless of the TiO₂ morphology on the catalyst surface, variations in deposition neutralizing agent clearly show that surface alkali on the catalyst is necessary to moderate the latent acidity/basicity of support materials in order to limit PO isomerization to propanal/acetone, respectively. There was not a clear advantage of one alkali over another observed; however, excess ammonium ions appear to promote the basic ring-opening of PO to acetone. Many metal-oxide supports may have too high a latent acidity/basicity and should not produce gold catalysts with high PO selectivity. The active oxygen species for epoxidation has been speculated to be peroxo or hydroperoxy species,^{3,8,2} and recently, hydroperoxy species have been observed on gold on titania catalysts.³² The presence of TiO₂ (or other metal oxides for that matter) in extended structures or octahedral coordination can catalyze the decomposition of said hydroperoxy species, resulting in HO• radicals³³ that then catalyze the nonselective oxidation of C₃H₆ or the further oxidation of PO to ethanal and CO₂. Submonolayer TiO₂-modified SiO₂, as well as TS-1-based catalysts, exhibited the smallest selectivities to ethanal and CO₂, which were the major decomposition products of PO.

The liquid-phase epoxidation of propylene has been examined extensively over a number of supports similar to those prepared in this work. While mixed titania-silicas and titania-dispersed-on-silica supports present industrially viable levels of activity using an organic peroxide as the oxidant,^{34–36} these same supports tend to decompose hydrogen peroxide, leading to inefficiency in the partial oxidation.³³ Hydrogen peroxide

selectivity was later found to improve with the dispersion of the titanium phase,^{34–36} culminating in the work of Clerici et al.,³⁷ in which propylene epoxidation proceeded over TS-1 with very selective utilization of hydrogen peroxide, ultimately leading to the assignment of activity to highly dispersed, tetrahedral titanium species.^{38,39} Although Tuel et al.⁴⁰ have subsequently shown that TiO₂ clusters consisting of six octahedrally coordinated titanium atoms supported on mesoporous silica are active and selective for the partial oxidation of aniline to azoxybenzene using hydrogen peroxide as the oxidant, the active titanium species, while not atomically, is still well dispersed. In addition to arguments previously made concerning the effect of titanium connectivity on catalyst deactivation, it cannot be ignored that the effectiveness of support tracks well with the liquid-phase reactivity using hydrogen peroxide. This, in conjunction with previous work using density functional theory⁴¹ showing peroxide formation over small gold clusters and experiments that have directly observed hydrogen peroxide formation⁴² or a hydroperoxy species³² over Au/TiO₂, lends credence to the assumption that gold acts to form hydrogen peroxide (or hydroperoxy species), which is then consumed in the epoxidation reaction in an identical manner in the gas and liquid phases.

5. Conclusions

The degree of titanium connectivity was systematically examined using catalyst supports ranging from rutile to isolated tetrahedral titanium in TS-1. As the degree of titanium isolation increases, both the conversion and selectivity benefit. As a result of the decrease in Ti–O–Ti entities, a significant improvement in selectivity is caused by a decrease in the cracking of propylene to ethanal and CO₂. As a result, gold supported on TS-1 was found to be both the most active and the most robust of the examined catalysts, followed closely by submonolayer titania on silica supports.

In a comparison between sodium carbonate, cesium hydroxide, and ammonium hydroxide, sodium carbonate was found to be the best compound for the neutralization of the gold deposition solution. In particular, catalysts produced using ammonium hydroxide resulted in higher selectivity to acetone, implying that the surface retained some basic character. The catalysts prepared with cesium hydroxide did retain some cesium ions following washing and calcination; however, the quantity of deposited Cs⁺ was too small to see a significant impact. Any effects due to the neutralizing agent had far less of an impact on reactivity than the overall titanium connectivity of the support.

Catalysts prepared on titania on silica supports were found to have superior reactivity and selectivity when the gold was deposited without calcining the support. An increase in the WHSV over these catalysts showed a significant increase in selectivity indicative of less PO consumption over the catalyst at shorter residence times. Catalysts prepared on uncalcined supports also benefited from oxidation and reduction treatments at 473 K, after which the overall TOF for PO changed only slightly, but the overall selectivity increased.

Catalysts prepared from citrate-stabilized, 2 nm gold colloids captured on submonolayer titania on silica supports were found not to benefit from calcination prior to reaction. Though substantial activity was not observed until after the reaction temperature reached 473 K, most likely the temperature at which citrate was removed from the surface, activating the catalyst on stream appeared to retain active sites that were destroyed by calcination.

Variations in titanium connectivity were ultimately found to track well with the relative stability of hydrogen peroxide on similar supports for the liquid-phase epoxidation of propylene, as taken from the literature. This adds to the mounting evidence that gold acts to produce hydrogen peroxide (or a hydroperoxy intermediate) and that the epoxidation reaction proceeds identically in the liquid-phase and gas-phase reactions.

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