Mechanistic Study into the Direct Epoxidation of Propene over Gold/Titania Catalysts

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The epoxidation of propene over gold/titania based catalysts was investigated using different techniques. Infrared spectroscopic information showed that one key step in the reaction mechanism is a reaction catalyzed by gold between titania surface groups and propene. In this reaction step, a bidentate propoxy species is formed on titania. This species adsorbs strongly on the catalyst, and it is the same species which is formed when propene oxide adsorbs on titania. Gravimetrical adsorption experiments and catalytic tests show that product adsorption and desorption are important factors determining the catalytic activity and the catalyst stability. By combining the information from different techniques, a kinetic mechanism is proposed.

1. Introduction

Propene oxide is one of the important building blocks in the chemical industry. The main products produced from propene oxide are polyols and polyurethanes. The major processes for propene oxide production currently in use have disadvantages. The chlorohydrin process is being phased out because of environmental concerns, since it involves chlorine chemistry producing chlorinated side products and calcium chloride. The other main process is the hydroperoxide process. Of this process, two versions exist, the propene oxide–*tert*-butyl alcohol (PO-TBA) process and the styrene monomer–propene oxide (SM-PO) process. These processes produce *tert*-butanol and styrene as respective coproducts in a fixed stoichiometric quantity, making the process less flexible toward market demands. A new DOW/BASF plant, which will produce propene oxide from hydrogen peroxide, is scheduled to become operational in 2008.[1] This process is based on the Enichem TS-1 catalyst.[2] A catalyst that can directly epoxidize propene using only oxygen or air with practical yields is not yet described in open literature. The traditional silver on α-alumina catalysts, which are used on a large scale in industry for the epoxidation of ethene, has a low selectivity for propene epoxidation, primarily because of the reactivity of the γ-hydrogen atoms.[3,4] A relatively new development for the direct epoxidation of propene is based on gold/titania catalysts which epoxidize propene using a mixture of hydrogen and oxygen under mild conditions. Although it similarly uses both hydrogen and oxygen, a process based on the gold/titania catalysts potentially is more attractive than the new DOW/BASF process, since it does not require the production of hydrogen peroxide out of hydrogen and oxygen first and thereby reduces the complexity of the process.

Seven years ago, gold on titania catalysts were reported for the first time by Haruta et al. as selective catalysts for the direct epoxidation of propene.[5] The original application of catalysts based on gold nanoparticles was low temperature CO oxidation.[6] Since that time, these catalysts have received a considerable amount of attention, resulting in about 100 publications until now.[7] The attention to these catalysts has not diminished, as is evidenced by the number of reports published by many groups

over the last year.[8–20] Despite all of this attention, the mode of operation of these catalysts is still under discussion, especially for the epoxidation of propene. Both gold and titania seem to be a necessity for a catalyst to be able to epoxidize propene. The fact that for this oxidation reaction both oxygen and hydrogen are necessary, as well as the fact that propene can be epoxidized by hydrogen peroxide over titania, makes the common assumption in the literature be that the reaction mechanism involves a peroxide species which would be produced by gold.[21–23] Theoretical calculations have shown that OOH[24] or even hydrogen peroxide[25,26] can be formed on gold particles. However, no evidence exists that shows this is also occurring during propene epoxidation, which makes this peroxide mechanism speculative.

Gold on titania catalysts still need considerable improvements to be made attractive for application in a large scale process. The main issues that need to be addressed are the activity, the hydrogen efficiency, and the catalyst stability.[27,28] Typically, at this time, the "normal" gold on titania catalysts have a propene conversion of up to 1% with a propene oxide selectivity of >95% and a hydrogen efficiency on the order of 30%. A key parameter for the catalytic activity is believed to be the gold particle shape and size. Haruta et al.[5,29] have shown that hemispherical gold particles of 2–5 nm in size are optimal for the epoxidation. Particles smaller than 2 nm catalyze the hydrogenation of propene to propane, due to different electronic properties of the gold. Particles which are too large have a relatively higher selectivity toward the combustion, most likely because of a loss in gold/titania interface when expressed per quantity of gold. Round gold particles are also less active, since they have a relatively smaller gold/titania interface. For CO oxidation, Chen and Goodman[8] showed that there is a large promotional effect for titania on gold when gold is deposited as a well-defined layer on it. For gold particles on a support, this effect will be largest when the surface area is largest, which supports the observation from Haruta.

For the gold/titania catalysts, an improved propene oxide yield can be obtained by using a support containing titania in a dispersed manner,[30] for which propene conversions up to 10% have been obtained at 90% selectivity, although the stability of the catalyst at this high conversion level needs to be improved significantly. Improved hydrogen efficiencies have been reported

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by using CsCl as a promoter.[31] Also, the modification of the titania surface by silylation of the hydroxyl groups to reduce the adsorption strength of the propene oxide produced is found to be beneficial for the product yield.[30] The improvements make it likely that in the future a gold/titania catalyst for an economically viable process can be found. The main advantage of such a process would be the simplicity of the direct oxidation in a single stage. The elucidation of the mode of operation of these catalysts is key to being able to make the needed improvements to the catalyst. This study therefore focuses on the reaction mechanism.

The main focus in this study is the investigation of the surface chemistry of a gold on titania catalyst in order to develop a reaction mechanism. Recently, we published a paper[9] elaborating on the role of gold in the activation of propene, based on the results of an infrared spectroscopic study on Au/TiO$_2$ catalysts. We showed that gold nanoparticles could induce the formation of an adsorbed bidentate propoxy species on titania. In this paper, these infrared experiments are extended to gold catalysts prepared on other supports and combined with catalytic data, gravimetrical adsorption/desorption data, and UV–vis and Raman spectroscopy. For this study, model catalysts composed only of gold on a support were prepared, without any of the known promoters or modifiers, to keep the catalyst as simple as possible. Surface reactions and adsorption of reactants and products on the catalyst and the supports were investigated. The spectroscopic information is linked to the catalytic information. The information collected from the different techniques is combined to present a mechanistic model for propene epoxidation over gold/titania catalysts.

2. Experimental Section

2.1. Catalyst Preparation. Catalysts were prepared with the following support materials: titania (P25, Degussa, 70% anatase, 30% rutile, 45 m^2/g), silica (Davisil 645, Aldrich, 295 m^2/g), and two types of titania dispersed on silica (Ti supported on Davisil 645 and on Degussa Aerosil OX50, 50 m^2/g).

In a rotating evaporator under a nitrogen atmosphere, 15 g of silica support was dispersed in 200 g of dry 2-propanol to which tetraethylorthotitanate (TEOT) was added. The quantity of TEOT added was chosen so that the titania loading would be well below a monolayer coverage on the silica (0.76 g for the Davisil 645 support, corresponding to 10% of a monolayer, and 0.27 g for the OX50 support, corresponding to 20% of a monolayer). The slurry was mixed by rotating the evaporating flask for 25 min. The 2-propanol was thereafter evaporated at 333 K at reduced pressure. The dry powder was calcined in air by first heating to 393 K (5 K/min) at which it was kept for 2 h and then heated at 10 K/min to 873 K. At this temperature, the support was held for 4 h and then cooled to room temperature.

Gold was deposited on the supports by means of a deposition precipitation method using ammonia.[22] [When preparing gold catalysts by a deposition precipitation method using ammonia, care should be taken that the possibility exists of the formation of explosive fulminating gold. In the preparations in this paper, the risks are very minor considering the small quantities of gold and the low loadings on the catalysts prepared. Care is advisable however considering a recently reported incident (Fisher, Gold Bulletin 36 (2003), 155). It is recommended that readers take the advantages (ease of making stable catalysts without chloride or sodium present) and disadvantages of this preparation method into consideration.] A 5 g portion of support was dispersed in 100 mL of demineralized water with a magnetic stirrer. The

pH of the slurry was 3.8 for the catalysts prepared on titania, 4–6 for the Ti–SiO$_2$ supports, and 7 for the silica support. Using 2.5% ammonia, the pH was raised to 9.5. A 77 mg portion of AuCl$_3$ was dissolved in 40 mL of demineralized water and added slowly for about 15 min to the support. While the gold solution was added, the pH was continuously adjusted so that it would remain between 9.4 and 9.6. After addition of all the gold, the solution was stirred for one more hour after which it was filtered and washed three times with 200 mL of demineralized water. The yellow catalyst was dried overnight in an oven at 333 K and then calcined. Calcination was carried out by heating to 393 K (5 K/min heating) for 2 h followed by 4 h at 673 K (5 K/min heating and cooling). The thus obtained catalysts had an intense dark color (dark purplish blue for the P25 support, brown for the Davisil support, bordeaux red for Ti–Davisil 645, and salmon pink for Ti–OX50).

2.2. Catalyst Characterization. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) micrographs were taken of the catalysts to determine the gold particle size and distribution on the catalysts. These analyses were combined with energy-dispersive X-ray (EDX) analysis to verify the composition of the particles observed and the homogeneity of the titania deposited on the silica support. X-ray fluorescence (XRF) analysis was used to determine the gold loading on the catalysts and the presence of contaminants effecting the activity (e.g., chloride). UV–vis diffuse reflectance spectroscopy measurements were done on the catalysts in an attempt to link the color to the metal particle size.

2.3. Catalyst Activity Testing. A flow reactor was used to determine the catalytic performance of the different catalysts. The experiments were carried out with typically 0.35 g of catalyst and a gas flow of 50 NmL/min (GHSV 9000 h^{-1}). The gas mixture consisted of 10% oxygen, 10% hydrogen, and 10% propene in helium (all gas compositions given in volume percent). The analysis of the gas leaving the reactor was carried out using an Interscience Compact GC system, equipped with a Molsieve 5A and a Porabond Q column, each with a thermal conductivity detector (TCD). Gas samples were analyzed every 3 min. The experiments were carried out in cycles: 5 h at a reaction temperature with the reactant mixture followed by a regeneration cycle. In a regeneration, 10% oxygen in helium was used and the catalyst was heated to 573 K (10 K/min) at which it was kept for 1 h, after which the catalyst was cooled to the next reaction temperature in the cycle. The performance was tested typically at 10–15 different temperatures (including duplicates to determine deactivation).

During the catalytic tests, optionally in situ Raman and UV–vis measurements were carried out in situ under reaction conditions. UV–vis measurements were done in the range 250–1100 nm using an Avantes Avaspec-2048-4 spectrometer. Raman measurements were done using a Kaiser RXN spectrometer equipped with a 532 nm laser. The setup used for these measurements is described in more detail elsewhere.[32]

2.4. Infrared Adsorption/Reaction Experiments. In a Perkin-Elmer Spectrum One infrared transmission spectrometer, adsorption experiments were performed using self-supporting catalyst wafers with a thickness of 100–120 μm (pressed at 1.5 t from powdered catalyst). Prior to the adsorption/desorption experiments, the samples were dried in situ by heating to 573 K in helium after which the samples were cooled to 323 K. For liquids, adsorption measurements were done by pumping 400 μL/h of liquid in a helium stream of 25 Nml/min (at 353 K) fed through the infrared cell for 10 min, after which only helium was fed and the desorption was measured. Propene adsorption

Epoxidation of Propene over Gold/Titania Catalysts

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was measured similarly with a gas stream of 5 Nml/min of propene in 35 Nml/min of helium. During the desorption in helium, spectra were measured until no changes were observed for at least 30 min. In the experiments, the empty cell was used as a background. Afterward, the spectra of the samples were recalculated using the sample at 323 K prior to the adsorption as a background. The bare titania used in the experiments was titania from a blank catalyst preparation (i.e., prepared identically as the gold catalyst but without the AuCl$_3$ added); therefore, differences in the adsorption behavior of propene can only originate from the gold and not from changes to the titania during the catalyst preparation.

2.5. Gravimetrical Adsorption/Desorption Experiments. The adsorption capacity for propene oxide was determined gravimetrically using a Perkin-Elmer Pyris 1 thermogravimetric analysis (TGA) balance for the catalysts and supports. Approximately 20 mg of sample was put into the balance, after which it was first dried in helium at 573 K and then cooled to 323 K. Subsequently, a gas syringe containing a 250 mL volume of helium saturated with propene oxide at 293 K was dosed to the sample (at 323 K) over a 40 min period. After flowing gas over the sample for 30 more minutes at 323 K, the temperature was increased to 773 K. The gas used in the final two stages of the experiment was either helium or 10% oxygen in helium. During the whole cycle, the mass of the sample was recorded.

3. Results

3.1. Catalyst Preparation and Characterization. TEM-EDX analyses of the Ti on SiO$_2$ supports showed that the titania was dispersed over the silica surface. No amorphous titania could be observed, and all EDX analyses showed the presence of titania on the silica. It was, however, not possible to determine if the titania was indeed dispersed over the support or present in smaller clusters. Raman analysis showed for both Ti−SiO$_2$ supports the appearance of a band at 950 cm^{-1} which is characteristic of Ti−O−Si vibrations.[33] A band at 144 cm^{-1}, characteristic of TiO$_2$ crystallites,[33] was not present.

XRF analysis showed that the gold loading on the catalysts was always close to the target loading. The gold loading was typically 75−95% of the target loading; the lower values were obtained for catalysts prepared using "older" gold(III) chloride, for which it was observed that a small amount of the gold precursor taken did not dissolve, as it had partially decomposed during air/light exposure in previous catalysts syntheses. The amount of chloride on the catalysts was below the detection limit (<6 μg/g).

TEM analysis shows that, for all supports used in this study, the gold particles were typically between 2 and 10 nm in size, with a maximum usually at 4−6 nm and a standard deviation of 1−2 nm. This indicates that for all supports used the interaction between the gold particles and the supports is similarly strong. A TEM micrograph for each of the two catalysts used most in the experiments, 1 wt % Au on P25 titania and 1 wt % Au on TiO$_2$ on OX50 silica, is shown in Figures 1 and 2, respectively. The few very large 20−30 nm dark particles visible in Figure 1 are titania particles stacked on top of other titania particles. In Table 1, the particle size information for the different catalysts is summarized. STEM-HAADF (scanning TEM using a high angle annular dark field detector) analysis performed on some samples produced an identical particle size distribution. EDX analysis using TEM on areas where no gold particles were visible did not show the presence of any gold. These observations indicate that no sub 1 nm "invisible" gold is present on the catalysts. This is also in agreement with the
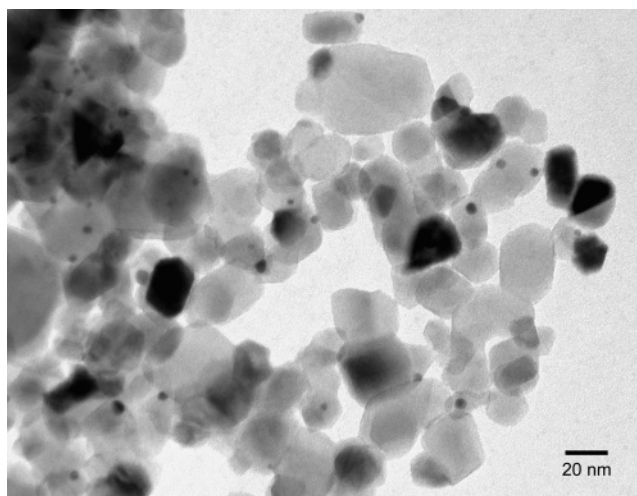

Figure 1. TEM micrograph of 1 wt % gold on P25 titania catalyst.
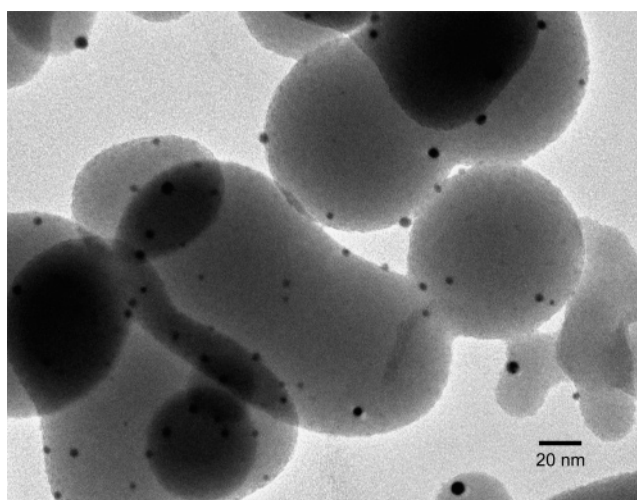

Figure 2. TEM micrograph of 1 wt % Au on Ti−OX50 catalyst.

shape of the particle size distribution curves, which goes down steeply from 3 to 2 nm.

The UV−vis spectra recorded for some of the catalysts prepared are shown in Figure 3. In this figure, the broad band at a wavenumber between 10 000 and 25 000 cm^{-1} is exclusively originating from the gold particles on the catalysts, since the UV−vis spectrum of the supports was used as a background. The maximum of this band (derived by taking the point where the first derivative of the curve equals 0) is also given in Table 1. For gold particles on the same support, the intensity of this band is directly proportional to the number of gold particles, as was evidenced from a series of Au/TiO$_2$ catalysts with a varying loading from 0.2 to 1 wt %. For these samples, the gold particle size according to TEM was similar. In UV−vis spectroscopy, the broad absorbance band was similar in shape and only the intensity varied in relation to the gold loading. In the literature,[34] it has been reported that the origin of this absorption is from the plasmon effect of the gold particles. It originates from the collective oscillations of the electrons at the surface of the nanoparticles, and therefore, it is affected by the particle size and the support with which the particles are in close contact. For light transmission through gold films, it has been shown that there is a linear relationship between the position of the maximum in the UV−vis transmittance and the thickness of the gold film.[35] For supported catalysts, we found that, when preparing gold catalysts at different pH values, the average gold particle size (from TEM) and the position of the absorbance

TABLE 1: Gold Particle Size on the Catalysts as Determined by TEM and Maximum in the UV−Vis Absorbance of the Gold Plasmon Band[a]

catalyst support	av particle size (nm)	standard dev in particle size	count (particles/ photographs)	UV−vis absorbance maximum (cm^{-1})
P25 (titania)	4.2	1.1	116/4	17 800
Davisil 645 (silica)	3.5	1.5	86/5	19 700
Ti on Davisil 645 (silica)	4.8	2.3	86/8	18 700
Ti on OX50 (silica)	4.8	1.8	121/4	19 300

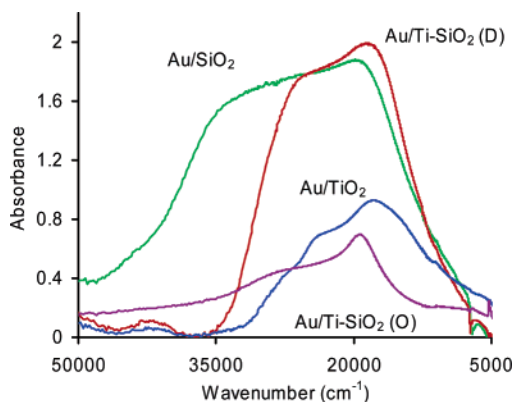[a] All catalysts have a 1 wt % loading of gold.

Figure 3. UV−vis spectra of supported gold catalysts. The spectra were recorded using the catalyst support as background. (Au/SiO$_2$, 1 wt % Au on Davisil 645 silica; Au/Ti−SiO$_2$ (D), 1 wt % Au on Ti dispersed on Davisil 645 silica; Au/Ti−SiO$_2$ (O), 1 wt % Au on Ti dispersed on Degussa OX50 silica; Au/TiO$_2$, 1 wt % Au on P25 titania).

maximum were connected: as the average particle size decreased, the absorbance maximum shifted to a lower wavelength. The UV−vis absorbance can therefore be used as a nice method to determine sintering of the gold particles. With respect to the position of the band originating from the gold particles, it can be seen that for the titania supported catalyst it is present at the lowest wavenumber and for the silica supported catalyst it is present at the highest wavenumber, with the position in between for the Ti−SiO$_2$ supported catalysts. Since, however, the average gold particle size is similar for all catalysts, it can be concluded that the interaction of the gold particles with the support is different. The different electronic properties of the gold as a result of this interaction cause a shift in the plasmon band as well as a difference in the intensity of the band.

3.2. Catalytic Testing. The catalysts were tested in 5 h cycles, with intermediate regeneration procedures. Although losses in catalytic activity could be observed within a cycle, the activity could be completely restored in the regeneration procedure at 573 K in oxygen/helium. Irreversible deactivation was not observed, not even after up to 20 catalytic cycles. In Figures 4 and 5, the catalytic performances are shown for the 1 wt % Au catalysts supported on P25 titania and on Ti−OX50.

Two major differences can be observed between the two catalysts. First, the optimal (highest propene oxide yield) reaction temperature is different; for a comparable conversion, the Ti−OX50 supported catalyst needs a higher reaction temperature. Second, within a 5 h catalytic cycle, the activity for the P25 supported catalyst first increases and then decreases rapidly (30%/h). For the Ti−OX50 supported catalyst the conversion does not exhibit a maximum and only decreases a lot slower with about 6−7%/h. In Table 2, the conversion, selectivity, and water production for a selection of reaction temperatures is summarized. The values are the averages from 30 to 270 min within one cycle and thereby especially for the titania supported catalyst significantly lower than the maximum activity which is commonly reported. For the titania supported

catalyst, unexpectedly, the conversion is lower at 373 K than at 323 K. This can be explained by the fact that at this temperature this catalyst deactivates much more rapidly than at 323 K. For catalytic experiments at intermediate temperatures, it is observed that, as the temperature increases, the time decreases at which the conversion curve crosses the curve measured at 323 K. Since the deactivation seems to be the result of a chemical reaction, rather than a change in the physical properties of the catalyst, this indicates that the activation energy for the deactivation is higher than that of the epoxidation.

The rapid deactivation makes it difficult to determine an apparent activation energy for the propene oxide production over the Au/TiO$_2$ catalysts. For the different gold catalysts supported on titanium dispersed on a silica support, apparent activation energies for propene oxide production were about 25−30 kJ/mol. The same value was obtained for the propene conversion. In Figure 6, an Arrhenius plot is given for an experiment over a Au/Ti−OX50 catalyst. It can be seen that at the highest temperature the data points for the propene conversion proceed on a straight line, while the apparent propene oxide production rate drops. This indicates that at higher temperatures the loss of selectivity toward propene oxide is due to a consecutive reaction and is not the result of a side reaction.

The main side products that are observed are water, carbon dioxide, methanol, acetone, propanal, and ethanal. Propane was not observed as a side product for these catalysts. However, catalysts prepared by deposition precipitation at a higher pH value, having smaller gold particles, did produce this side product.[36] The apparent activation energy for water production for all catalysts prepared was between 33 and 40 kJ/mol. For catalysts with a similar gold particle size, it was found that the water formation rate was similar for all catalysts, independent of the support, indicating water formation primarily occurs over the gold particles. These values are in good agreement with the theoretical values of Barton and Podkolzin[24] for density functional theory (DFT) calculations for water formation over gold nanoparticles.

The two catalysts supported on a titania−silica support have different activities, although the activity trend for these two catalysts is the same. Since the gold particle size is the same for both catalysts, the difference in activity must originate from the support. The difference in the position of the maximum of the plasmon band for the gold particles measured by UV−vis spectroscopy indicates that the interaction between the gold particles and the support is different, which can be part of the explanation for a difference in activity. Since the activity of the catalyst originates from both the gold and the titanium in the support, also differences in the support itself can cause this difference in activity. The main differences between the two titania−silica supports are the surface area (50 m^2/g for Ti−OX50 and 295 m^2/g for Ti−Davisil 645) and acidity (pH 4.2 for Ti−OX50 and pH 5.9 for Ti−Davisil 645 for 6 g of support/100 mL of demineralized water).

The UV−vis measurements during the epoxidation did not show any changes in the spectrum during the experiments,
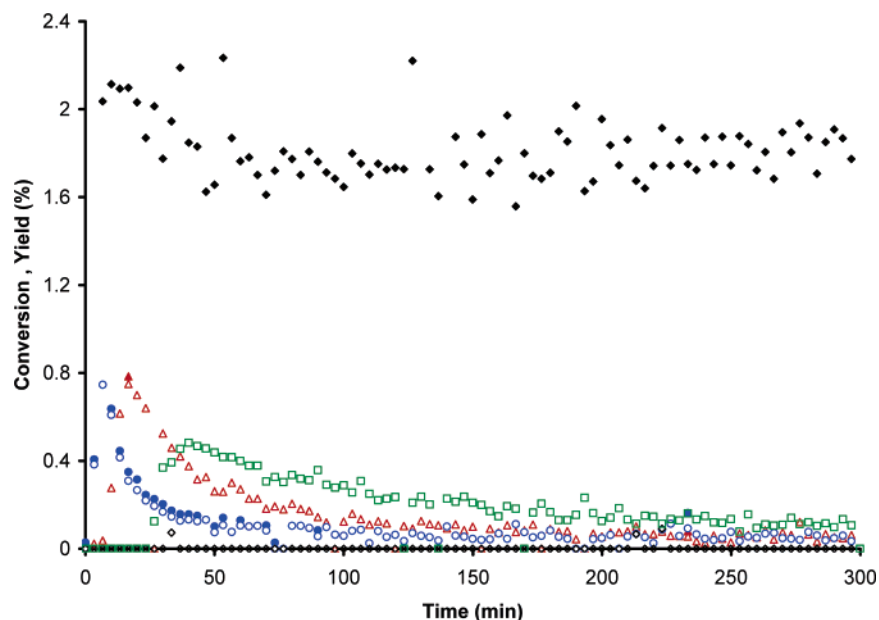
Figure 4. Catalytic performance of the Au/TiO$_2$ catalyst. Conversion (closed symbols) and yield (open symbols) at 323 (□), 343 (△), 363 (○), and 423 K (◇). Pressure, 1 bar; GHSV, 9000 h^{-1} (note that the conversion and yield data points largely overlap for the 323 and 343 K experiments).
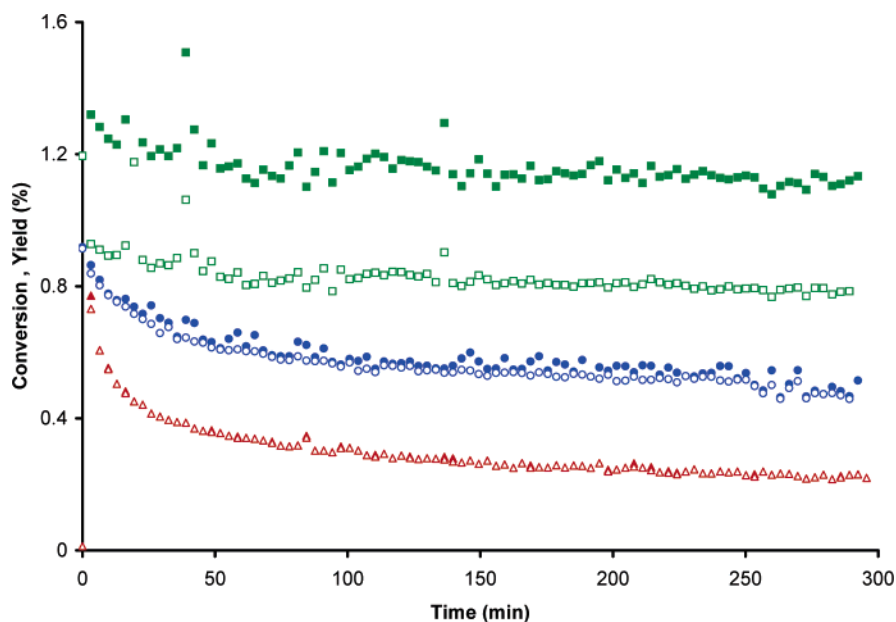

Figure 5. Catalytic performance of the Au/Ti−OX50 catalyst. Conversion (closed symbols) and yield (open symbols) at 373 (△), 408 (○), and 448 K (□). Pressure, 1 bar; GHSV, 9000 h^{-1}.

TABLE 2: Summary of the Catalytic Performance of the Catalysts (Selectivity for Gas Phase Products)^a

catalyst	conversion (%)				selectivity (%)				hydrogen efficiency (%)			
	323 K	373 K	423 K	473 K	323 K	373 K	423 K	473 K	323 K	373 K	423 K	473 K
1% Au/TiO$_2$	0.23	0.07	1.8	3.8	>99	95	0.2	0	12.2	2.4	0.04	0
1% Au/SiO$_2$	0	0	1.1	2.5			12	21	0	0	0.2	0.5
1% Au/Ti on Davisil	0.12	0.37	0.83	2.9	96	96	87	27	6.0	10.0	7.1	2.7
1% Au/Ti on OX50	0.04	0.25	0.80	1.8	>99	>99	90	42	5.6	19.7	13.5	4.2

^{a} Average conversions and selectivities from 30 to 270 min within an epoxidation cycle. GHSV 9000 h^{-1}.

indicating that the gold particle size (distribution) remains unchanged. Figure 7 shows the very broad and intense Raman bands in the region 1300−1600 cm^{-1} that appear in the reactions performed using Au/TiO$_2$ catalysts. Typically, these types of Raman bands originate from cokelike species on the catalyst. An accurate identification of these species, however, could not be made. Both propene and propene oxide caused the formation of these bands; feeding oxygen/helium without propene or

propene oxide made these bands disappear. For reactions using a catalyst with gold on a Ti−SiO$_2$ support, these broad Raman bands were not observed. Raman bands of peroxide type species (expected at approximately 900 cm^{-1}) could not be observed in any of the experiments. Also, adsorbed propene or propene oxide could not be observed on the catalyst. This was partly because of the very low Raman signal because of the very dark color of the catalyst and partly because of the high intensity of
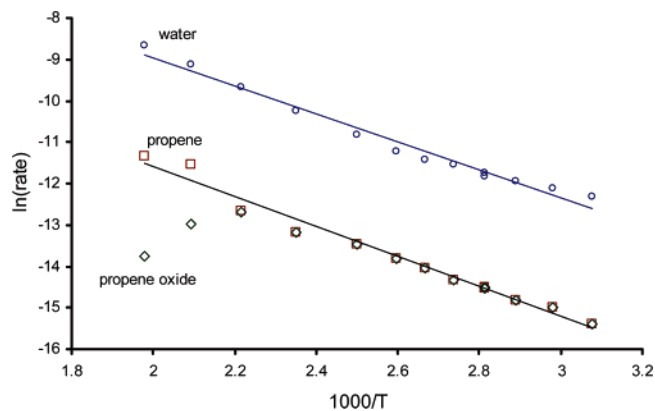
Figure 6. Arrhenius plot of rates (mol/g_{cat}/min) of propene conversion and propene oxide and water formation over a 1 wt % Au/Ti−OX50 catalyst. Pressure, 1 bar; GHSV, 9000 h^{-1} (conversion values average over 30−270 min reaction time).
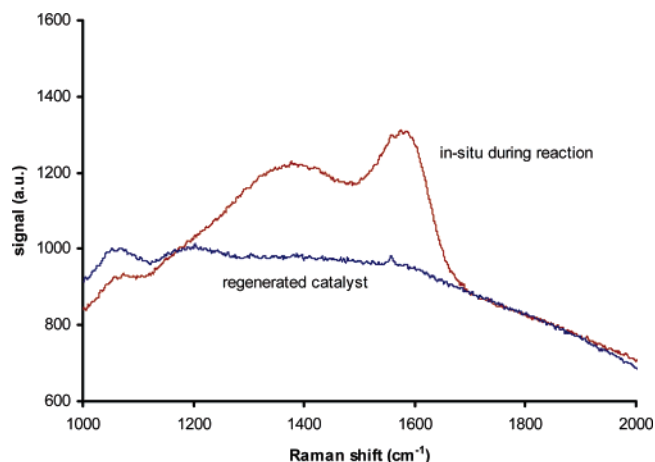

Figure 7. Raman bands appearing during propene epoxidation over a Au/TiO$_2$ catalyst (323 K, 1 bar, GHSV 9000 h^{-1}).

the Raman signal from 1300 to 1600 cm^{-1}. Only for Raman measurements on the bare supports, for which the Raman signal obtained is much higher because of the white color, adsorbates could be seen. These adsorbates are similar to those observed in the infrared adsorption experiments discussed in the next section.

3.3. Infrared Adsorption/Reaction Experiments. When the adsorption and subsequent desorption of propene on the bare titania P25 support is measured, no bands remain present on the titania, indicating a completely reversible physical adsorption. However, when the same experiment is performed with the Au/TiO$_2$ catalyst, the adsorption is no longer reversible. In Figure 8, the spectra of both samples after the desorption of physisorbed propene are shown. The residual species on the surface of the Au/TiO$_2$ catalyst are clearly visible. On the other hand, for titania, only a small decrease for the absorption at 1650 cm^{-1} is seen caused by a slightly decreased water content, which also causes the negative background at the higher wavenumbers. For the gold on titania catalyst, bands have appeared at 2970, 2935, 2870, 1460, 1440, 1375, 1340, 1130, and 1090 cm^{-1}.

The bands in the 1050−1150 cm^{-1} region are most likely characteristic of C−O−Ti stretching vibrations.[37,38] This indicates that an adsorbed species remains on the titania support. To make the identification of this residual species more facile, experiments were performed in which different components were adsorbed and desorbed on the P25 support. Propene oxide, 1,2-propanediol, 1-propanol, and 2-propanol all adsorbed ir-
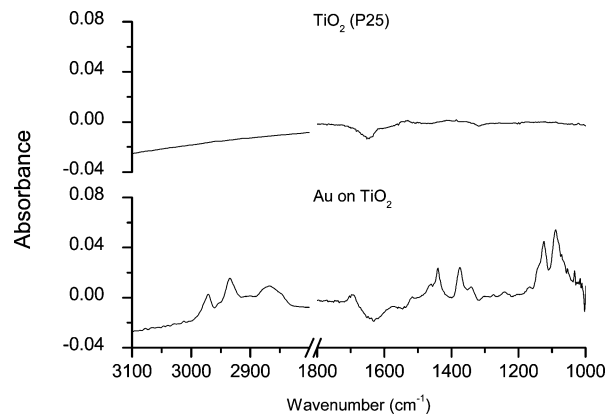

Figure 8. Infrared spectra of adsorbed species on titania support and gold on titania catalyst after adsorption and subsequent desorption of propene (323 K) (100 spectra averaged).

reversibly on (reacted with) titania. The spectra of species remaining after adsorption/desorption are given in Figure 9A. In the CH stretching region, the main bands that can be observed are usually assigned as ν_{as} for CH$_3$ at 2970 cm^{-1}, ν_{as} for CH$_2$ at 2935 cm^{-1}, ν_s for CH$_3$ at 2900 cm^{-1}, and ν_s for CH$_2$ at 2870 cm^{-1}. In the CH bending region, δ_{as}CH$_3$/δCH$_2$ at 1460 cm^{-1}, δ_sCH$_3$ at 1375 cm^{-1}, and δCH at 1335 cm^{-1} can be assigned. The bands at 1090 and 1140 cm^{-1} can be assigned as the C−O−Ti stretching vibrations for primary and secondary carbon atoms, respectively. The structures of the most likely species as they are formed on the titania surface are given in Figure 9B. The observed spectra for the adsorption of these reference components are very similar to those published by Mul et al.[37] when they adsorbed the same species on gold/titania. The only difference is that they observed that these species were oxidized on the catalyst to ketones (band at 1700 cm^{-1}), which we did not observe. This can be explained by the absence of gold in our reference measurements performed on the bare support.

When the difference spectrum after propene adsorbed/desorbed on the gold on titania catalyst in Figure 8 is compared to the spectra in Figure 9, it can be seen that it is very similar to that of the species on the surface of titania after adsorption of propene oxide or propanediol. The source of the oxygen in this component is unclear, but most likely, it originates from titania O or OH groups. The formation of this species can only be explained by considering a key role of gold: most likely, propene adsorbs on gold and this adsorbed and activated species then reacts with surface O(H) of the titania. Alternatively, gold may influence the reactivity of the nearby titania, making it react more easily with propene. The fact that the peak intensities of the spectrum in Figure 8 are relatively low (absorbance 20 times lower than those in Figure 9) can be easily explained by the relatively low gold loading of 1 wt %. Since without gold no irreversible propene adsorption occurs, it is a reasonable assumption that in the presence of gold the adsorption still will only occur in the immediate surrounding of a gold particle. In Figure 1, it can be seen that the gold particles only occupy a small portion of the titania surface.

The only real difference between the spectrum in Figure 8 and those in Figure 9 for adsorbed propene oxide and 1,2-propanediol are the peak intensities of the bands at 1440 and 1370 cm^{-1}. Over time, the intensity of these bands increases further even if the catalyst is kept in a helium gas stream, while the intensity of the other bands decreases very slowly (Figure 10). At 1500−1550 cm^{-1}, a broad band also appears. These increasing bands can be attributed to carbonate/carboxylate species.[39,40] The fact that the intensity of the CH stretching bands
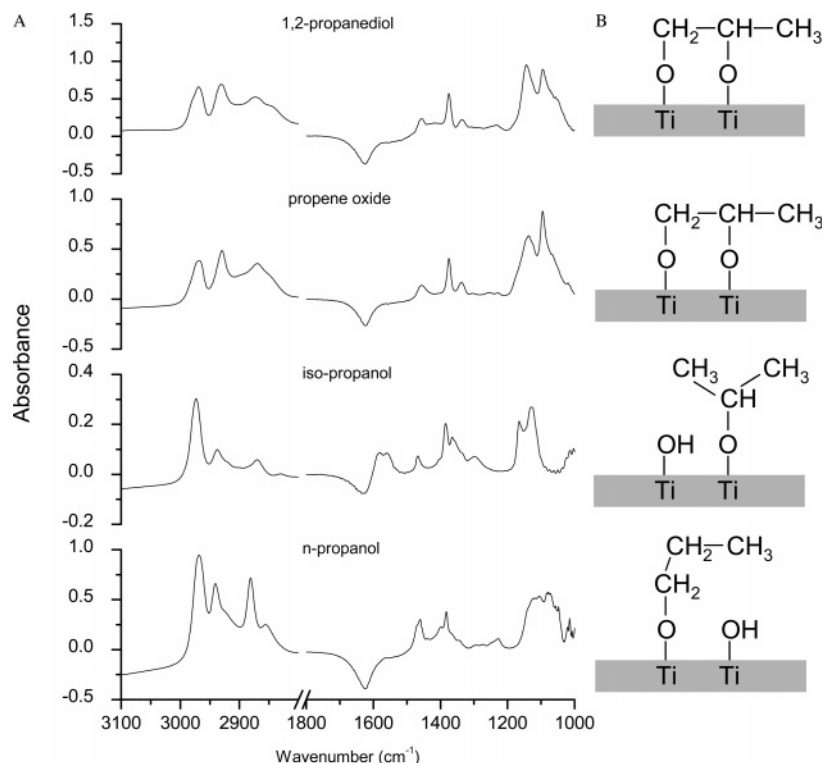
Figure 9. (A) Infrared spectra after adsorption and subsequent desorption of 1,2-propanediol, propene oxide, 2-propanol, and *n*-propanol on titania (323 K). (B) Most likely adsorbate species corresponding to the infrared spectra in part A (20 spectra averaged).
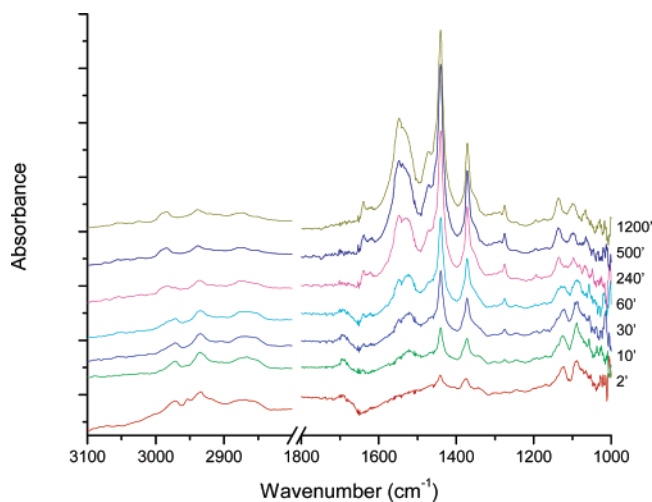

Figure 10. Spectra showing gradual oxidation of bidentate propoxy species on a gold/titania catalyst. The spectra were recorded 2−1200 min after exposure of the catalyst to propene for 2 min (323 K) (10 spectra averaged).

does not increase supports this assignment. The formation of carbonates/carboxylates can be explained by a slow oxidation of the bidentate propoxy species. This oxidation reaction must be catalyzed by the gold particles, since it is not observed when the bidentate propoxy species is formed on bare titania by adsorption of propene oxide or 1,2-propandiol. This slow formation of carbonates/carboxylates might be part of the reason the gold/titania catalysts slowly lose activity during the epoxidation. The fact that a calcination procedure removes these species from the surface agrees with the observation that the catalyst largely regains its activity for the epoxidation after calcination. Additional evidence that these carbonate/carboxylate species are key to the deactivation of the catalyst comes from the fact that they could not be observed on a catalyst consisting of gold on a dispersed titania support (Au/Ti−OX50), which

does not show the fast deactivation that the titania supported catalysts exhibit.

An additional experiment was performed in which 10% propene was fed to the Au/TiO$_2$ sample for only 3 min in a gas stream containing 10% oxygen and 10% hydrogen. The presence of hydrogen and oxygen results in much more intense bands of the bidentate propoxy species in a shorter time. Similar to what is shown in Figure 10, in the presence of hydrogen/oxygen, it is observed that the bidentate propoxy species is slowly oxidized on the catalyst surface; in this case, however, the bidentate propoxy bands decrease in intensity more rapidly, indicating desorption is occurring. Increasing the temperature to 373 K results in the complete disappearance of the bands of the bidentate propoxy species (only the carbonate/carboxylate bands remain), which was not the case if a similar experiment was performed in a helium stream. This indicates that hydrogen and oxygen aid in the desorption of this species, possibly by producing a peroxo species. It is very unlikely the desorption occurs via the formation of water from hydrogen and oxygen, since in gravimetrical experiments it was observed that adsorbed water could be displaced by propene oxide but adsorbed propene oxide (bidentate propoxy) could not be displaced by water. Furthermore, catalytic experiments showed that only the presence of both hydrogen and oxygen could yield propene oxide as a product.

It should be noted that Mul et al.[37] did not observe the formation of the bidentate propoxy species when propene was adsorbed on a similar gold/titania catalyst. A clear explanation for this difference cannot be given. Our experiments were easily reproducible. Also, possible contaminants (like propene oxide or alcohols) in part of the setup could be ruled out as a cause of the bidentate propoxy formation, since the bidentate propoxy was observed being formed out of propene over a gold/titania catalyst, while it could not be observed in an immediately preceding experiment in which propene was absorbed on bare titania. An explanation for why Mul et al. could not make the
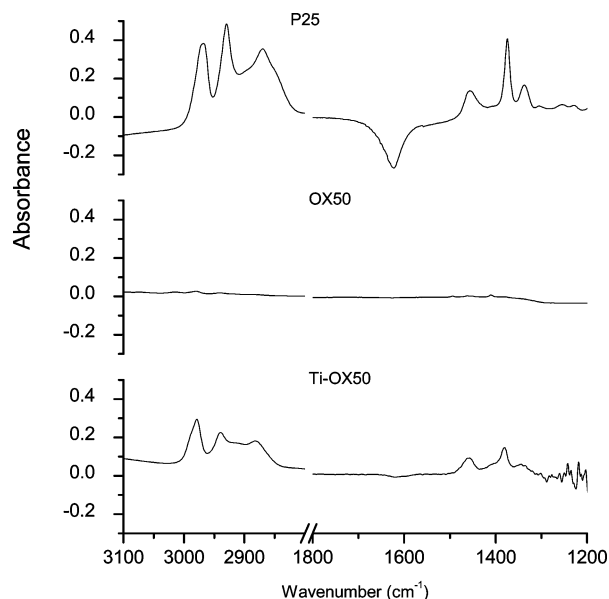
Figure 11. Propene oxide adsorption followed by desorption in helium for different catalyst supports: P25 TiO_2, OX50 SiO_2, and Ti dispersed on OX50 SiO_2 (measured at 323 K) (20 spectra averaged).

same observation might be one of the following. First, their catalyst pretreatment temperature prior to the experiments was 393 K versus 573 K in this study, which might have caused a different water content. Second, the average particle size of the gold nanoparticles in this study was somewhat smaller (4.2 nm average size with 2−6 nm range versus observed particle range from 3 to 6 nm[41]). Finally, the gold/titania catalyst of Mul et al. already contained clearly observable hydrocarbon species on the surface prior to propene absorption, which might well have obscured the low intensity bands from the bidentate propoxy species that we observed. The fact that Mul et al. did not observe the bidentate propoxy species formation directly out of propene made them conclude that this species was not a reaction intermediate but just adsorbed propene oxide. However, similar to us, they did link this species to the catalyst deactivation. They considered the bidentate propoxy to be the deactivating species, together with the acetates and formate species formed out of it as it is oxidized further. Since we consider the bidentate propoxy species itself to be a reaction intermediate, we only consider those species that are formed out of it after further oxidation to be deactivating.

In Figure 8, a small band is visible at 1700 cm^{-1}. In Figure 10, this band can be seen to be appearing in the first minutes after the propene adsorption and then disappearing again. This band can be assigned to a C=O stretching vibration.[37] The fact that this band first appears and then disappears indicates that a ketone or aldehyde species is formed out of the adsorbed bidentate propoxy species as a first step in its oxidation on the catalyst surface.

To get an understanding of the similarities and differences between the titania supported catalysts and catalysts supported on titania dispersed on silica, propene oxide adsorption experiments were carried out. In Figure 11, the irreversibly adsorbed propene oxide is shown on titania, silica, and Ti−SiO_2. The difficulty with the silica support is that the transparency for infrared radiation is too low below 1300 cm^{-1}, obscuring the C−O−Ti or C−O−Si bands. However, it is easily seen that on the bare silica support no irreversibly adsorbed propene oxide remains present. For the propene oxide absorbed on Ti−SiO_2, the vibrations of the adsorbed species are very similar to those of the bidentate propoxy species adsorbed on titania; all
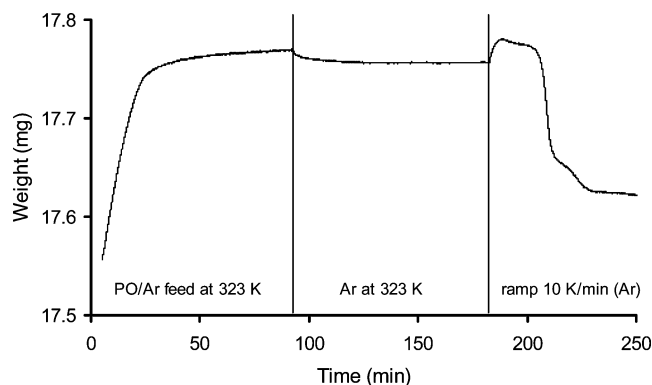

Figure 12. Example of a thermogravimetrical adsorption/desorption experiment. Adsorption of propene oxide on P25 titania in an argon atmosphere.

vibrations are only shifted to a higher energy by 10 cm^{-1}, suggesting the formation of a similar bidentate propoxy species. For the shift of the infrared bands to a higher energy, there are two possible explanations, between which at this time no choice can be made.

The first possibility is that the bidentate propoxy species is bonded to a Si atom and a Ti atom for the Ti−OX50 supported catalyst but is bonded to two titanium atoms for the titania supported catalyst. Actually, two varieties of such species would be possible, with the Ti bonded to the primary carbon atom and the Si bonded to the secondary carbon atom and vice versa. In this case, doublet peaks would be expected, which is not the case, indicating a kinetic/thermodynamic preference for one of these species rather than the other. The second option is that the bidentate propoxy species is still bound to two titanium atoms but that the vibrations are shifted due to the somewhat different properties of the titanium atoms, since it is no longer in a titania support but in/on a silica surrounding. This second option is somewhat less likely than the first considering that the catalyst has only a relatively low titanium loading (theoretical 10% of monolayer coverage) and the intensity of the vibrations of the bidentate propoxy species is quite high.

For the gold catalyst supported on Ti on silica (Ti−OX50), feeding propene only to the catalyst also caused the formation of a small amount of irreversibly adsorbed species on the catalyst. The intensity of the signal, however, was about 10 times lower compared to that of the bidentate propoxy produced from propene over gold/titania, which can be explained by the much lower titania content and the supposition that the active site consists of both gold and titania. For this catalyst, the Ti(Si)−O−C vibrations are not visible due to the lack of transmittance of the silica, making identification of the species difficult. However, the presence of an irreversibly adsorbed species indicates that the reaction mechanisms for the titania supported and Ti−SiO_2 supported catalysts are similar.

3.4. Thermogravimetrical Analysis. In Figure 12, an example is shown for a thermogravimetrical adsorption/desorption experiment. In the three parts of the experiments, it can be seen that in first part the fast irreversible adsorption of propene oxide occurs (producing the bidentate propoxy) followed by a slower physisorption. In the second step in argon, the physisorbed propene oxide desorbs. In the heating phase in argon, the bidentate propoxy is decomposed on the surface, which in the absence of oxygen leaves behind a small amount of carbonaceous species. The small weight increase at the beginning of the heating phase is a characteristic of the equipment used; also, for an empty sample holder, the weight increases by a total of 0.08 mg upon heating. Table 3 gives the adsorption

Epoxidation of Propene over Gold/Titania Catalysts

J. Phys. Chem. B, Vol. 109, No. 41, 2005 **19317**

TABLE 3: Summary of Thermogravimetrical Adsorption Experiments[a]

catalyst support	gas	relative weight change after (%)		
		adsorption (323 K)	desorption (323 K)	desorption (773 K)
P25 (titania)	argon	+1.50	+1.42	+0.36
P25 (titania)	20% O_2 in argon	+1.50	+1.40	−0.14
Au/P25	argon	+1.42	+1.31	+0.03
Au/P25	20% O_2 in argon	+1.52	+1.41	−0.16
Ti on OX50 (silica)	argon	+0.59	+0.45	+0.11
Ti on Davisil 645 (silica)	argon	+2.07	+0.88	−0.41
Davisil 645 (silica)	argon	+4.41	+0.34	−1.21

[a] Adsorption of propene oxide gas at 323 K followed by desorption (first isothermal at 323 K, then heating to 773 K, values corrected for mass changes recorded in a blank run).

capacity for the different samples. The main observations that can be made are that gold does not change the adsorption capacity of propene oxide and that only when the catalyst is heated in an air stream, the catalyst regains its original weight. Heating in an argon stream results in a catalyst of which the net weight has increased. Therefore, it can be concluded that the adsorption of propene oxide is not reversible. When the temperature programmed desorption in air of propene oxide is compared for the presence and absence of gold, it can be seen that during heating there is a small weight increase compared to the sample in the absence of gold, which agrees with the observation from the infrared adsorption experiments, which showed that gold could oxidize adsorbed species.

When the adsorption on silica and Ti−SiO$_2$ is considered, it can be seen that the physisorbed quantity (as long as PO is being fed) is considerably higher due to the adsorption of propene oxide on silica. After desorption at 323 K, already most of the adsorbed propene oxide desorbs. Heating the sample further results for both of these samples in a complete desorption of all adsorbed propene oxide.

4. Discussion

4.1. Catalytic Activity. For the titania supported catalyst, an activity going through a maximum is observed. This can be explained with the aid of the infrared and thermogravimetrical adsorption experiments. These experiments show that propene oxide adsorbs very strongly on the catalyst. In the infrared experiments, we also see that the adsorbed propene oxide is oxidized to carbonates/carboxylates. On the basis of our observations using the infrared experiments, we have the following phenomena occurring on the catalyst: (1) production of propene oxide from propene on catalytic gold/titania sites, (2) desorption of propene oxide from catalytic sites aided by hydrogen/oxygen, (3) adsorption of propene oxide on catalytic sites, (4) adsorption of propene oxide on noncatalytic titania sites, (5) oxidation of propene oxide adsorbed on catalytic gold/titania sites to carbonates/carboxylates.

In short, this summarizes the three processes occurring on the catalyst: reaction of propene to propene oxide, accumulation of propene oxide on the surface, and deactivation by a side/consecutive reaction. In the part of the experiment where propene oxide is detected as a product, the accumulation of propene oxide on the titania surface is complete (i.e., the maximum adsorption capacity is reached). This makes it possible to make an extrapolation of the propene oxide concentration as it would be without this adsorption having occurred, that is, how it would be if deactivation would be the only factor. One can then integrate the area between this curve and the curve describing the actually observed quantity of propene oxide, which provides a number for the adsorbed PO on the catalyst. For the propene epoxidation over Au/TiO$_2$ at 323 K, it was

calculated that approximately the equivalent of 0.7 wt % (0.6−0.9 wt % range of reasonable estimates) propene oxide would have been "left behind in the reactor" adsorbed on the catalyst. This number agrees well with the observed amount of strongly adsorbed propene oxide determined in the thermogravimetrical experiment shown in Table 3 for the same catalyst. Looking at the catalytic experiments for the catalyst prepared on the Ti−SiO$_2$ support, we do not see the behavior of the titania supported catalysts. The deactivation rate of the catalyst is much lower, and also, the concentration at the reactor exit does not increase at first; its highest value is reached almost immediately. This can be explained using the infrared and thermogravimetrical experiments. For this support, the adsorption of propene oxide is considerably less. For this support, most of the propene oxide on the catalyst desorbs immediately after the propene oxide atmosphere is removed.

4.2. Catalyst Deactivation. The gold catalysts used in this study all exhibit a tendency to deactivate. This deactivation ranges from severe for titania supported catalysts (dropping to about 20% of its maximum activity after 5 h of operation, 325 K) to relatively mild for Ti−SiO$_2$ supported catalysts (losing about 25% of its activity after 5 h of operation, 408 K). This deactivation, however, is completely reversible as far as it can be observed on a time scale of up to 10 days. Once the catalyst has been regenerated at 573 K in an air stream, the catalytic activity is completely restored. Even after up to 30 reaction/regeneration cycles, no differences can be seen in either conversion or selectivity of the catalyst. In the previous paragraph, the assumption was made that the deactivation within one cycle is caused by the formation of carbonates/carboxylates at the catalytic sites from adsorbed propene oxide by gold. This is a likely assumption considering that the activity can be restored by a relatively low temperature calcination.

The conversion of the adsorbed bidentate propoxy species to carbonates/carboxylates, leading to deactivation, only occurs on the titania sites neighboring the gold particles. When an experiment is carried out in the infrared cell in which propene oxide is adsorbed on a gold/titania catalyst, it can be seen that only a very small portion (a few percent) of the adsorbed bidentate propoxy species is oxidized. Although this cannot be proven from the experiments performed, it is a likely assumption that these are the same species as those that are being oxidized in Figure 10, namely, those bidentate propoxy species adjacent to the gold particles.

4.3. Catalytic Mechanism. The catalytic mechanism for this reaction requires the presence of both gold and titanium (as TiO$_2$ or Ti dispersed on or in an oxidic support). Titania alone has no activity for the epoxidation of propene with hydrogen and oxygen. Gold on silica does not produce significant quantities of propene oxide either. Some other metals cooperating with titania also have some epoxidation activity, but their perfor-

mance is considerably worse than that of gold. Only silver is now showing some promise for this reaction system.[42,43]

In the literature,[22,23] a peroxide species is commonly assumed to be a key reaction intermediate in the propene epoxidation using hydrogen/oxygen over gold/titania catalysts. The expectation that such a species would be a key reaction intermediate is primarily because of the good epoxidation activity titania catalysts have when a peroxide is used as an oxidant.[2] A peroxide species, however, has not been observed in our studies using infrared and Raman spectroscopy, even though Raman spectroscopy is known to be quite sensitive toward peroxides. Product desorption is the reaction step, which according to our observations and earlier reports[22,28] would be rate determining. The predominant species on the catalyst surface should therefore be adsorbed propene oxide, which can be present in the form of the bidentate propoxy we observe. A peroxide species can still play a key role in the reaction mechanism, considering our observation that hydrogen and oxygen aid the desorption of the bidentate propoxy species. If one would assume that peroxide needs to be formed to aid the desorption of the propene oxide/ bidentate propoxy, and that the formation of this peroxide species would be the rate-determining step, this does imply that the concentration of the peroxide species is very low. As a consequence, the concentration of this peroxide species might simply be beyond the sensitivity of our equipment. The peroxide formation on gold from hydrogen and oxygen has been confirmed in the literature both theoretically[24,25] and experimentally.[23,44] This supports a reaction model in which a peroxide species is formed on the gold particles in the rate-determining step, which reacts with the bidentate propoxy species to produce propene oxide. Such a model is able to explain our experimental observations. The kinetic isotope effect for hydrogen−deuterium substitution reported by Stangland et al.[21] confirms the assumption of a peroxide species formation being a rate-limiting step. In their isotope experiments, they concluded that hydrogen should be bonded to a reaction intermediate playing a role in the rate-limiting step. For the production of hydrogen peroxide over gold catalysts,[45] it was shown that this reaction is first order in hydrogen and limited by the activation of hydrogen on the catalyst. This is in agreement with our model and the observed kinetic isotope effect.
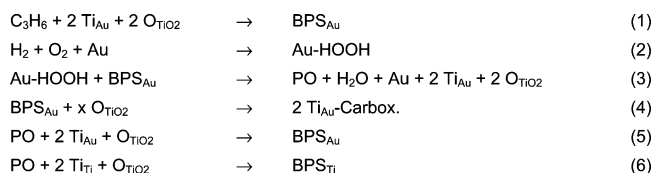
Therefore, the reaction mechanism we would like to propose is the following:

(1) Propene reacts with titania to produce an adsorbed bidentate propoxy species. This reaction is catalyzed by the gold nanoparticles present on the titania.

(2) Hydrogen and oxygen produce a hydroperoxide species on gold.

(3) The peroxide species aids in the desorption of the bidentate propoxy species from the catalyst, producing propene oxide and water and restoring the titania in its original state.

A question for the first step of this reaction mechanism, however, is what is the oxygen source for the bidentate species that we are forming on the catalyst surface. In the infrared propene adsorption experiments, this species was formed without the presence of oxygen in the gas phase. The oxygen source therefore must be the titania. It is known that titania can be reduced or donate oxygen under relatively mild conditions.[46,47]

In Scheme 1, the reaction mechanism, as derived from our experimental observations, is shown for propene epoxidation over gold/titania catalysts. As discussed earlier in this section, reaction 2, the formation of the peroxide species is most likely the rate-determining step. A kinetic reaction model based on this mechanism could be fitted successfully to the experimental

SCHEME 1: Model Representing the Key Steps in Propene Epoxidation over Gold/Titania Catalysts

$C_3H_6 + 2\,Ti_{Au} + 2\,O_{TiO2}$	$\rightarrow$	BPS_{Au}	(1)
$H_2 + O_2 + Au$	$\rightarrow$	$Au\text{-}HOOH$	(2)
$Au\text{-}HOOH + BPS_{Au}$	$\rightarrow$	$PO + H_2O + Au + 2\,Ti_{Au} + 2\,O_{TiO2}$	(3)
$BPS_{Au} + x\,O_{TiO2}$	$\rightarrow$	$2\,Ti_{Au}\text{-}Carbox.$	(4)
$PO + 2\,Ti_{Au} + O_{TiO2}$	$\rightarrow$	BPS_{Au}	(5)
$PO + 2\,Ti_{Ti} + O_{TiO2}$	$\rightarrow$	BPS_{Ti}	(6)

With:		
	C_3H_6	gas phase propene
	BPS	bidentate propoxy species
	Ti	Titania site (Ti-O-Ti or Ti-OH)
	O	lattice oxygen
	PO	gas phase propene oxide
	Carbox	carbonate / carboxylate / formiate species

Subscripts:		
	Au	neighboring gold particle
	Ti	on the bulk titania, not neighboring gold
	TiO_2	(oxygen) originating from the titania support

observations, yielding realistic values for rate constants and activation energies.[48]

5. Conclusions

A mechanistic model, developed by combining catalytic, spectroscopic, and sorption data, is presented for propene epoxidation over gold on titania catalysts. Infrared spectroscopy has shown that gold is capable of activating propene or titania in such a way that a bidentate propoxy species is formed on the titania. This species desorbs aided by hydrogen and oxygen, which most likely form a peroxide species over gold in the rate-determining step. Infrared and gravimetric experiments have shown that the propene oxide produced can adsorb irreversibly on titania, which causes an "induction" period for the catalytic activity. Catalyst deactivation is most likely caused by a catalytic oxidation by gold of the bidentate propoxy reaction intermediate.

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Epoxidation of Propene over Gold/Titania Catalysts

J. Phys. Chem. B, Vol. 109, No. 41, 2005 **19319**

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