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The role of support oxygen in the epoxidation of propene over gold–titania catalysts investigated by isotopic transient kinetics

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ABSTRACT

Transient kinetic experiments were performed on gold–titania catalysts for the epoxidation of propene using hydrogen and oxygen to investigate the reaction mechanism. A 'classical' 1 wt% gold on titania catalyst was studied, as well as a 1 wt% gold on Ti-SBA-15 catalyst. Steady-State Isotopic Transient Kinetic experiments using oxygen-18 were performed, which provide information on the types and quantities of species present on the catalyst during reaction, as well as on possible reaction pathways.

The isotopic transients of the reaction products take place on a time scale of minutes, while the isotopic switch of the unreacted feed gases proceeds in a matter of seconds. This indicates that the oxygen pool on the catalysts, either in the form of adsorbed products or in the form of oxygen available for the reaction, is large in comparison to the product formation rates. The results indicate that support oxygen is playing a role in the reaction mechanism, but this could not be determined conclusively. For the water produced as a side product, it could be determined that support oxygen is ending up in the water; however, this can be explained by an exchange after its formation. The size of the oxygen pool in the neighborhood of gold, calculated based on the size of the TEM visible gold particles, is smaller than the amount of oxygen that ends up in the carbon containing oxidation products, which indicates that most likely part of the gold is present in sub-nanometer particles, not visible by TEM.

1. Introduction

For the epoxidation of propene, catalysts consisting of gold nanoparticles on a titanium-containing oxidic support have attracted considerable attention over the past years [1–3]. These catalyst systems are generally highly selective and moderately active, but they also suffer from a low stability and a low efficiency toward hydrogen, which is used as a co-reactant. An excellent review on gold catalysts is given by Hashmi and Hutchings [4].

Gold–titania catalysts are a highly attractive alternative to directly produce propene oxide [5]. Propene oxide is an important chemical intermediate, which is produced annually by as much as 6 Mtons, with demand still increasing. All current processes (SM/PO, PO/TBA, Sumitomo, Chlorohydrin, and DOW/BASF HPPO) are quite complex, which require multiple reactions and reactors with many separations. The gold–titania based catalysts, however, perform the reaction in a single step at mild conditions. Co-feeding hydrogen together with oxygen and propene is essential for the catalytic activity of these catalysts.

The gold–titania catalysts are bifunctional, both titanium oxide and gold need to be present to have a significantly active hydro-epoxidation catalyst [6]. The general consensus in the literature is that the primary role of the gold particles is to produce a peroxide species, which is thereafter used to epoxidize propene over a titanium site. This is supported by the fact that gold nanoparticle catalysts are capable to directly produce hydrogen peroxide [7–9]. In the liquid phase titanium- based catalysts, especially TS-1, are very efficient epoxidation catalysts using hydrogen peroxide as an oxidant [10]. Using UV–vis [11] and XANES [12] spectroscopic measurements it has indeed been observed for gold–titania catalysts that the peroxide species produced on the gold nanoparticles are transferred to titanium sites. In addition, Nijhuis et al. [6,13] observed that even in the absence of gas phase oxygen, gold particles catalyzed the formation of partially oxidized species on the titania surface (bidentate propoxy species). This formation is explained by propene that is adsorbed on the gold nanoparticles [14]. One thing which was not clear is if these partially oxidized surface species would be intermediates toward propene oxide or simply spectators or even deactivating species.

In this study, the Steady-State Isotopic Transient Kinetic Analysis (SSITKA) technique [15,16] is used to investigate the role of support oxygen in the propene epoxidation mechanism. In the SSITKA

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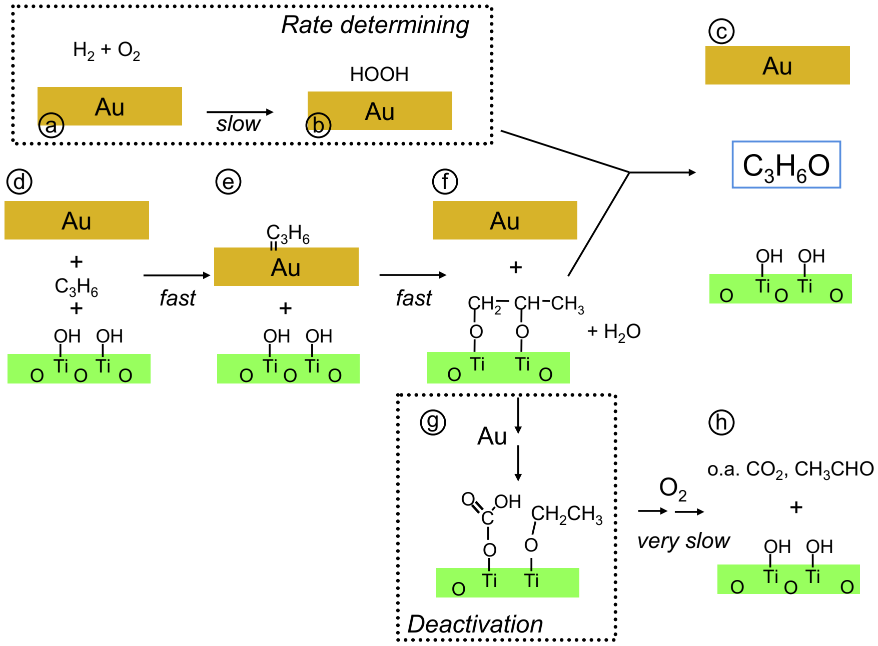
technique, a catalyst is used in a catalytic experiment under constant reaction conditions – ideally at steady state. At one point during the experiment, the feed is switched for an identical feed, but with one (or more) of the reactants substituted for the same reactant containing an isotopic version of one of the atoms in it. In this case, oxygen-18 was used to substitute non-labeled oxygen-16. By examining the time and rate at which the labeled oxygen appears in the products, mechanistic information could be obtained and the amount of adsorbate species on the catalyst can be calculated. A big advantage of this technique is that the amount of adsorbate species determined, is the amount of species involved in the reaction mechanism, and does not include spectator species, as can be the case for spectroscopic techniques. Spectator species that interact slowly with reaction intermediates, for example (sub)surface oxygen of the catalyst which exchanges with products or reaction intermediates, will result in SSITKA responses that are tailing. It should be noticed that in the experiments only direct information is obtained on the hold-up of oxygen on the catalyst surface and its movement through the reaction sequence. In the interpretation of the data, we will link the oxygen-containing species observed to specific types of adsorbates. However, the technique does not give evidence on the lifetime and quantity of the carbon-containing species, with respect to these species the evidence is indirect and based on the assumption that all reaction products are produced in the most likely direct manner possible. The delay times that we observe in the SSITKA response are not a direct function of the rates of reactions, but rather determined by the oxygen pool size or number of adsorption sites divided by the reaction rate.

In the discussion of the results from the SSITKA experiments, we will be trying to match the observations to the mechanistic scheme (Scheme 1), which we developed based on our previous work. A key species in this mechanism is the bidentate propoxy species (f). We observed the formation of this species using in situ infrared spectroscopy [6,13]. This species is formed on a gold–titania catalyst when it is exposed to propene, even in the absence of hydrogen and/or oxygen. The oxygen in this bidentate propoxy species should, therefore, originate from the support. Bidentate propoxy species are only formed on a titania support when these are exposed to propene, when gold nanoparticles are present. We explained this by adsorbing propene first in an activated manner on the gold nanoparticles (e), which we observed using in situ XANES experiments [14]. We observed [6,13] that the bidentate propoxy species (f) could only be removed from the support (c), when we exposed the catalyst to hydrogen and oxygen. This observation is the main reason why we assume this species is an intermediate and not a spectator, although it is clear this is not direct evidence. We assume that this reactive desorption was aided by peroxo species, which multiple researchers have reported that it can be produced on gold nanoparticles [7–9]. The rate of the desorption of the bidentate propoxy species is most likely determined by the rate of formation of the peroxide species. Using in situ infrared experiments, we also observed [6,13] that the bidentate propoxy species could be oxidized further by the gold nanoparticles to strongly adsorbing species (g) (e.g. carboxylates), which desorb slowly or can be removed by heating the catalyst in air to 573 K. We assume that these species are the primary cause for the loss in catalyst activity within a single experimental run. A reaction kinetic model based on these spectroscopic experiments described the observed catalyst performance well [17,18]. The mechanism of the Au/Ti-SBA-15 catalyst for the propene epoxidation is assumed to be similar to that of the Au/TiO_2 catalyst. The main difference is the dispersed nature of the Ti on the support. The bidentate propoxy species is formed linking to a Ti and a Si atom, which is less strongly bonded to the support [19]. Oyama et al. [20,21] presented an alternative mechanism for the epoxidation over gold on titanosilicate-supported catalysts. In their mechanism, the peroxide produced on gold is transferred to a titanium site, which then directly produces propene oxide from propene via a Langmuir–Hinshelwood mechanism.

2. Materials and methods

SSITKA experiments [22] were performed on two types of gold nanoparticle catalysts. The first type consisted of 1 wt% of gold on titania (P25). The preparation and performance of this catalyst are discussed by Nijhuis et al. [6]. The second catalyst is a 1 wt% gold on Ti-SBA-15 catalyst (Si/Ti = 40, ammonia treated), prepared according to Sacaliuc-Parvulescu et al. [23]. Both the catalysts were



Scheme 1. Mechanism proposed for the epoxidation of propene over a gold–titania catalyst. (Adapted from Nijhuis and Weckhuysen [18] using new insights from [14]).

run at their respective optimal reaction temperature (323 K for Au/TiO_2 and 423 K for Au/Ti-SBA-15), at which they have a comparable epoxidation activity (1.0 µmol/min and 2.7 µmol/min respectively). The experiments were performed with 0.3 g catalyst, diluted with 1.5 g of silicon carbide to have a uniform temperature in the catalyst bed. The temperature indicated for the experiments was the actual temperature of the catalyst bed. By calculating the Weisz-Prater and the Mears criterion, both in- and external mass transfer were determined to be absent, which is consistent with the similar calculations in the literature [24].

The gas feed during the SSITKA experiment consisted of 10 vol% of propene, hydrogen, and oxygen in argon. Specifically, 30 ml/min argon was fed with 5 ml/min propene and 5 ml/min hydrogen directly to the reactor. In addition, 5 ml/min argon together with 5 ml/min $^{16}O_2$ was fed to the reactor through a rapid switching valve. After running the reaction at constant conditions for 30 min, the gas feed going through the switching valve was exchanged for 5 ml/min $^{18}O_2$ with 5 ml/min neon to determine the SSITKA transient for oxygen in the feed. The switch of a small amount of argon for neon was made to determine possible peak broadening of the pulse response due to the dispersion in the catalyst bed and the gas lines. The system is designed in such a manner that it is possible to instantly make a switch from one gas feed to another, without disturbances in pressure or flow. This was done by utilizing a fast 4-way switching valve shortly before the catalyst bed, the non- selected gas flow was allowed to stabilize well before the switch was made, going to a vent line in which a pressure controller kept the pressure identical to the pressure before the catalyst bed. In this manner, the vent line pressure was identical to the reactor line pressure and the pressure of the isotopic feed line was identical to that of the non-isotopic feed line. The rise time for the inert neon tracer from 10% to 90% was approximately 3 s, which does include the peak broadening due to the dispersion in the catalyst bed.

The SSITKA experiments were run for a total of 20 min using $^{18}O_2$, to limit the consumption of the expensive gas. The product analysis was performed using both a mass spectrometer and a gas chromatograph–mass spectrometry (GC–MS) system. The mass spectrometer was used to scan all major m/e (mass over charge) values for the most relevant components, with a time resolution of 2.5 s for each component. The GC–MS system was equipped with a 16 position gas sampling valve. The sampling valve filled sample loops from the moment the isotopic switch was made until 20 min afterwards, initially with a 30 s interval, which was increased after each loop was filled. After all sample loops were filled, they were analyzed on the system. The analysis of the experiments was only performed in a quantitative manner with respect to the isotopic composition of the major products, propene oxide, carbon dioxide, and water. The system was not calibrated for the total quantitative amounts of the product. The quantitative performance of the catalysts tested using the SSITKA analysis was determined in a dedicated set-up and had been published previously [6,14,23,25]. By combining the catalytic performance of the catalysts with the isotopic composition for each of the products, determined using the SSITKA experiments at identical conditions, a quantitative analysis of the surface species could be made.

3. Results

The characteristics of the system were evaluated by examining the response of neon. Fig. 1 shows the mass spectrometer response for neon, measured at a higher mass spectrometer sampling rate (measuring less m/e signals). It can be seen that the gas composition switch travelling through the catalyst bed is complete in about 3 s. Broader transients measured during the catalytic experiments will be caused by phenomena (adsorption, reaction, and desorption) at the catalyst surface.

Fig. 2 shows the transients during the epoxidation for propene oxide, water, and carbon dioxide during the epoxidation over Au/TiO_2. Fig. 2, as well as the other figures displaying the SSITKA transients (Figs. 4–6), gives the fraction of the isotopic varieties of the products related to the total amount of that product produced. The isotopic transients for the products are very slow. The isotopic switch from $^{16}O_2$ to $^{18}O_2$ was made after 40 min of running the epoxidation, which is close to the point where the epoxidation rate is the highest (see Fig. 3). For both water and carbon dioxide, even after 15 min, the most predominant isotopic species produced ($H_2{}^{16}O$ and $C^{16}O_2$) only contained ^{16}O. To evaluate if this very slow transient would be caused by a strong adsorption on the catalyst, or by a large pool of oxygen containing intermediates on the

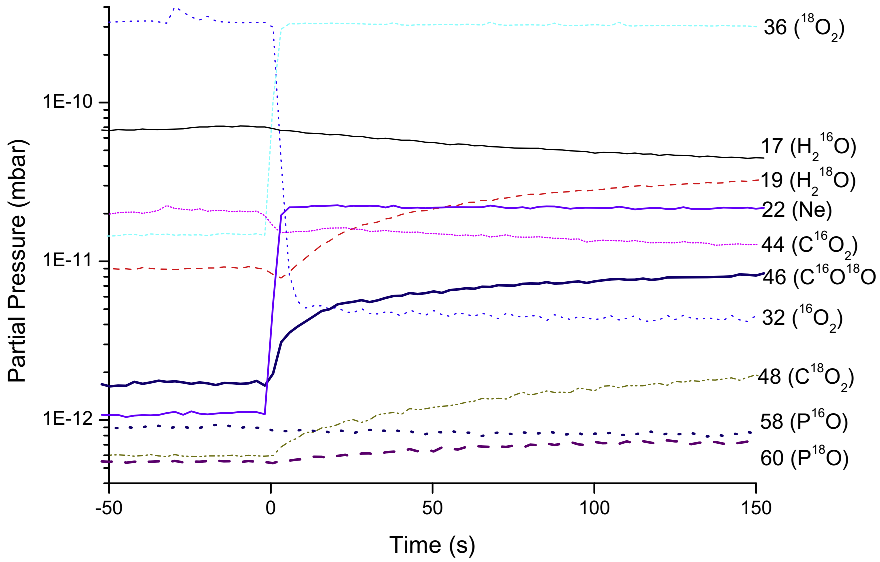


Fig. 1. Example of SSITKA transient data recorded with Mass spectrometer upon making the isotopic switch at $t = 0$. From the Ne signal, the peak broadening due to the catalyst bed/system can be determined. Switch from $^{16}O_2$ to $^{18}O_2$ after running the propene epoxidation over a 0.3 g of 1 wt% Au/Ti-SBA-15 catalyst at 423 K for 40 min (50 Nml/min total flow rate, 10 vol% of H_2, O_2 and propene in Ar/Ne).

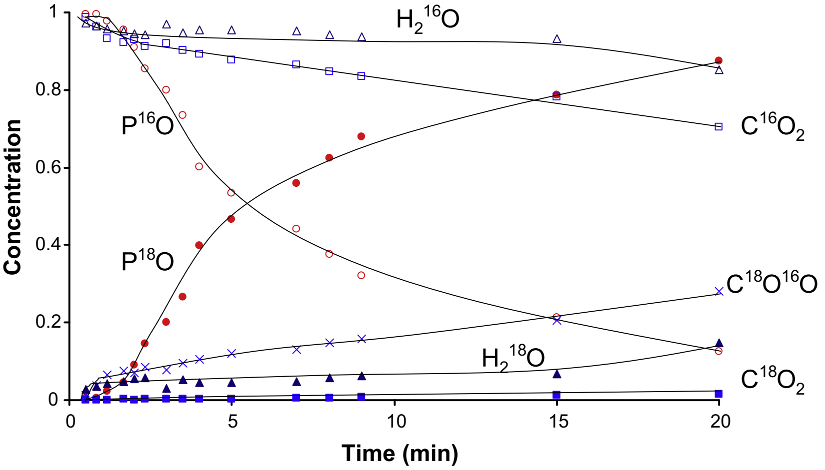


Fig. 2. SSITKA transients for switch from $^{16}O_2$ to $^{18}O_2$ (at $t = 0$) after running the propene epoxidation over a 0.3 g of 1 wt% Au/TiO_2 catalyst at 323 K for 40 min (50 Nml/min total flow rate, 10 vol% of H_2, O_2 and propene in Ar/Ne). Isotopic fractions for the products are given normalized to the amount of all isotopic varieties of the product produced at that moment.

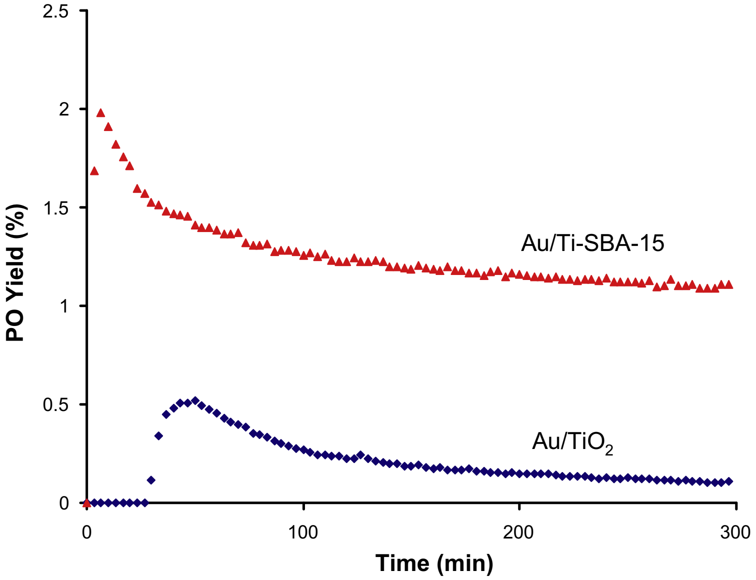


Fig. 3. Catalytic performance of Au/TiO_2 (323 K) and Au/Ti-SBA-15 (423 K) catalysts at their optimal reaction temperature (1 wt% Au loading, 0.3 g catalyst, 50 Nml/min total flow rate, 10 vol% of H_2, O_2 and propene in He, 1.1 bar(a)).

catalyst, an additional experiment was performed in which over the same catalyst a SSITKA switch was performed from $^{12}CO_2$ to $^{13}CO_2$ (in argon/neon). This experiment is shown in Fig. 4. The almost instantaneous switch shows that the delays observed in Fig. 2 are not caused by adsorption on the catalyst of the carbon dioxide produced, but rather by a slow release/production rate. The fact that in Fig. 2 the amount of $C^{18}O_2$ produced after 15 min is still less than 1% of the CO_2 production, indicates that gas-phase oxygen does not play a direct role in the release of this product from the catalyst. It can be concluded that the size of the oxygen pool supplying the CO_2 is significantly larger than the rate of CO_2 formation. A possible explanation for this can be that either carbonates are released slowly from the catalyst, or support oxygen is ending up on the CO_2 produced.

The isotopic transients for the Au/Ti-SBA-15 catalyst are shown in Fig. 5. It can be observed that for this catalyst, the transients are much faster than those for the Au/TiO_2catalyst, but the transients are significantly longer than the actual gas switch breakthrough time of about 3 s. The SSITKA switch for the Au/Ti-SBA-15 catalyst was similar as for the Au/TiO_2 catalyst made after operating it in the epoxidation for 40 min. At this moment, the activity of the catalyst was constant.

4. Discussion

The isotopic transients for the products in the epoxidation over both the Au/TiO_2 (Fig. 2) and the Au/Ti-SBA-15 (Fig. 5) catalysts are slow. This can be explained in two ways. A first explanation is that the reaction products are produced on the catalyst surface and only desorb slowly. A second explanation is that the oxygen fed in the gas phase does not directly appear in these products, but is converted first into a different oxidizing species (e.g. a hydroperoxide), which has a significant retention/coverage on the catalyst surface. For the carbon dioxide produced, which contains two oxygen atoms, we can draw one further conclusion from the experiments. Since a large quantity of single labeled carbon dioxide is produced

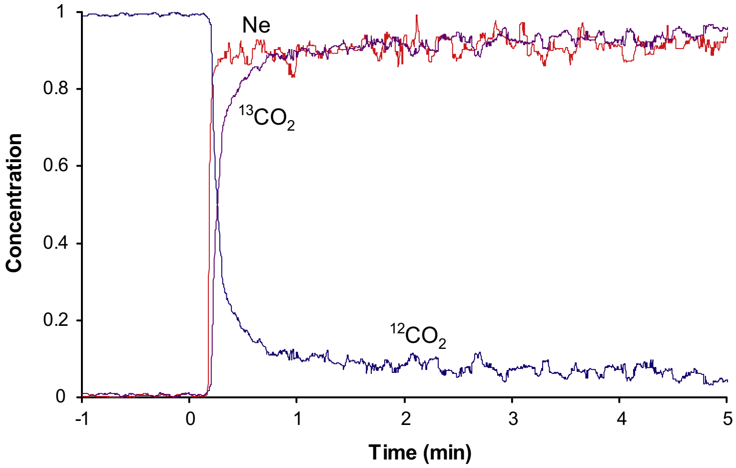


Fig. 4. SSITKA response for a CO_2 isotopic switch over 0.5 g of 1 wt% Au/TiO_2 catalyst. Switch from $^{12}CO_2$ to $^{13}CO_2$ isotopes at $t = 0.323$ K. Total flow rate 60 ml/min, 2 vol% CO_2 in Ar (Ar/Ne after switch). CO_2 composition scaled to 1, Ne transient scaled from 0–1 for transient.

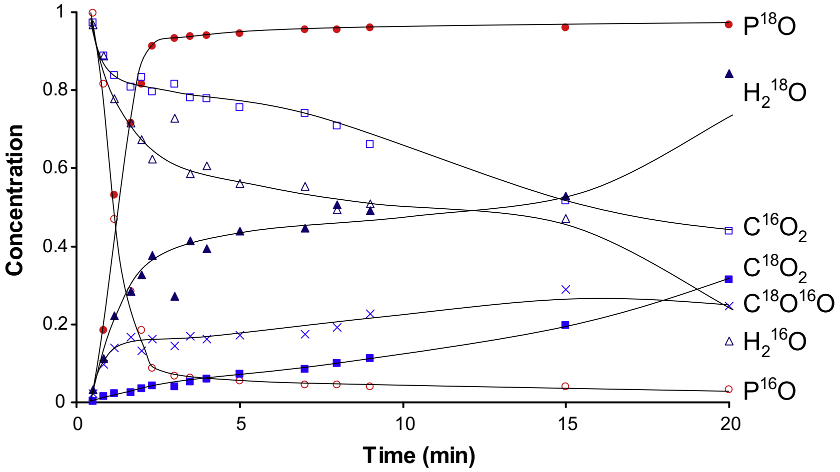


Fig. 5. SSITKA transients for switch from $^{16}O_2$ to $^{18}O_2$ (at $t = 0$) after running the propene epoxidation over a 0.3 g of 1 wt% Au/Ti-SBA-15 catalyst at 423 K for 40 min (50 Nml/min total flow rate, 10 vol% of H_2, O_2 and propene in Ar/Ne).

over a longer time, this implies that it is formed in a two-step oxidation. After the SSITKA switch, single labeled CO_2 is produced almost instantaneously, even faster than ^{18}O containing propene oxide. This indicates that a partially oxidized species is oxidized further either directly from oxygen in the gas phase, or from a rapidly formed oxidizing surface species (adsorbed atomic oxygen, adsorbed molecular oxygen, or a peroxo species). The fact that for a long time $C^{16}O_2$ is the dominant type of carbon dioxide, indicates that in addition an adsorbed CO_2 precursor, which does not need further gas-phase oxygen to be provided for its production, is also present in a significant amount on the catalyst. Since CO_2 adsorption itself on the catalyst is only minor (Fig. 4), a slow decomposition of a surface carboxylate species can be the explanation for this slow response. The fact that even while $C^{16}O_2$ is still the primary type of CO_2 produced, after 20 min for the Au/Ti-SBA-15 catalyst $C^{18}O_2$ is produced/released in a larger amount than single labeled $C^{16}O^{18}O$, which is an indication that at least two routes are present producing carbon dioxide. In case all CO_2 produced would be originating from a single oxygen pool (route), statistically it would be impossible that both $C^{16}O_2$ and $C^{18}O_2$ would be produced in a larger quantity than $C^{16}O^{18}O$ (in a single perfectly mixed oxygen pool with $C^{16}O_2$ and $C^{18}O_2$ released at the same rate, statistically the amount of $C^{16}O^{18}O$ released should be twice the concentration of $C^{16}O_2$ (or $C^{18}O_2$)). Combined with the above mentioned fact that the first $C^{16}O^{18}O$ could be observed before $P^{18}O$, it can therefore be concluded that one of the (at least) two oxygen pools from which carbon dioxide originates is relatively small. The formation of single labeled carbon dioxide is a good indication for a two or more step formation, since both oxygens are not originating from the same gas-phase oxygen molecule. Such a step-wise oxidation of propene is also present in the mechanistic Scheme 1 we present, in which propene is first partially oxidized to a bidentate propoxy species. This partially oxidized species can be non-selectively oxidized further to surface oxygenates (g), which are finally oxidized further to carbon dioxide (for the Au/TiO_2 catalyst carbon dioxide is the only observed carbon containing side product).

Based on our previous in situ infrared studies and kinetic investigations, we have proposed a reaction mechanism for the epoxidation of propene over gold–titania catalysts. This mechanism is shown in Scheme 1 [18]. In this scheme, a first step in the epoxidation is the formation of a bidentate propoxy species on the catalyst support. It should be noted that although we propose that this bidentate propoxy species is a true reaction intermediate [6,13], this has not yet been proven. The oxygen in the bidentate propoxy species was thought to be coming from the catalyst support. The main argument for this proposition was that we observed the formation of this species using infrared spectroscopy upon exposing a gold–titania catalyst to propene in the absence of oxygen in the gas phase [6,13]. Our current observations are in agreement with this first step in the mechanism. Since the titania-supported catalyst has a large amount of oxygen in the support available, the appearance of 18-oxygen in the propene oxide support can be delayed for a long time. The Ti-SBA-15-supported catalyst only has a relatively small amount of reducible titania present, which explains why labeled oxygen appears a lot faster in the propene oxide produced. An additional explanation for this difference is a decreased adsorption strength of the bidentate propoxy species [19] when it is formed on a catalyst with titania dispersed on/in a silica support. In this case, the bidentate propoxy species is only able to interact with one Ti-site, with the other 'leg' of the bidentate species binding to a Si. It should be noted, however, that even though the current SSITKA observations are in agreement with our previously published scheme with respect to the formation of the bidentate propoxy species, it is not proving that the bidentate propoxy species is indeed an intermediate. For example, in case oxygen adsorbed on the gold nanoparticles would be exchanging with oxygen from the support, similar SSITKA responses as are visible in Figs. 2 and 5 will be obtained.

Deactivation of the catalyst, as well as formation of carbon dioxide, was explained in our previous work by a consecutive oxidation of the bidentate propoxy species [6,13]. The oxidized species formed would be strongly adsorbed on the catalyst and only desorbed slowly. In the SSITKA experiments, we do indeed observe that the isotopic transient for the titania-supported catalyst is extremely slow. In the mechanism given in Scheme 1, it can be observed that as the C–C bond between the two legs of the bidentate propoxy species is broken in the route toward complete oxidation, two partially oxidized species are produced. The consecutive oxidation and desorption of these two species at different rates can be the explanation for the minimum of two routes toward CO_2 formation that we identified from the SSITKA.

For the titania-supported catalyst, it is clearly visible in Fig. 2 that $H_2{}^{18}O$ is observed as a product prior to ^{18}O labeled propene oxide. This indicates that at least part of the water produced is a primary product, while propene oxide is not. This is in agreement with the common idea that first hydrogen peroxide is produced, which thereafter epoxidizes propene over a titanium site, and also with our proposed alternative route in which hydrogen peroxide (Scheme 1) is required for the reactive desorption of propene oxide from the catalyst. The fact that $H^{18}O_2$ appears prior to $P^{18}O$, however, can also be used as an argument for the more common view in the literature that H_2 and O_2 would produce H_2O_2, which would thereafter epoxidize propene. The initial fast appearance of $H^{18}O_2$ is an indication of a fast incorporation of the ^{18}O in the reaction pathway responsible for its formation (either direct, or as coproduct for propene oxide) in a relatively small oxygen pool, the slow path toward a complete isotopic transient (only $H^{18}O_2$) is an indication of an interaction of this oxygen pool with a much larger oxygen pool, for example via an exchange with support oxygen.

To make a semi-quantitative interpretation of the adsorbates playing a role during the reaction, we extrapolated the SSITKA transients to completion (i.e. a complete switch of the oxygen atoms in the products to oxygen-18). These extrapolated curves are shown in Fig. 6. The area under these curves was determined, in this way providing a hold-up for the respective species on the catalyst. The curves were drawn in such a manner that we think they sooner underestimate the size of the oxygen pools than overestimate them. These hold-ups for the species on the catalysts are for actual reaction intermediates and will not include spectator species, because of the nature in which SSITKA experiments are performed, spectator species remaining inactive on the catalyst surface are not observed. The integrated areas under the extrapolated curves might have a relatively large error, since the extrapolations are just made 'by eye', but they will provide a good indication for the amount of these species. In Table 1, these areas are given. For the three isotopic versions of carbon dioxide, the amounts were calculated by a mix of extrapolating the individual isotopic varieties and a molar balance that the three types together would be summed to 1.

By taking the catalytic activity of the catalysts (conversion and selectivity) into consideration, the SSITKA areas in Table 1 can be converted to absolute molar amounts adsorbed by multiplying the SSITKA areas (min) by the reaction rates (μmol/min). In Table 2, the relevant information on the catalytic performance of the catalysts is given, as well as the amounts of adsorbates that were calculated from these values and the SSITKA transients. The 'adsorbates' calculated in this manner might in reality not represent a single adsorbate species, but it does reflect the size of an oxygen pool involved in the formation of the corresponding product. For the calculation of the adsorbed amounts, the amounts of produced products containing ^{16}O after the switch to $^{18}O_2$ are used (from Table 1). In case support oxygen is playing a role in the reaction; however, the calculated values for the adsorbates would be too high, since ^{16}O from the support can end up in the product. The amounts of 'adsorbates' calculated in this manner should, therefore, be compared to the number of available sites for reaction and adsorption to make a determination whether it is likely if these species are indeed adsorbates or if they would be produced by surface oxygen. Table 3 lists the most important physical characterization data on the catalysts and the number of sites that can be calculated from this data.

When a comparison is made between the amount of $P^{16}O$, which leaves the catalyst after the SSITKA switch (7.9 μmol for the TiO_2-supported catalyst and 5.5 μmol for the Ti-SBA-15-supported catalyst), and the number of titanium sites on both catalysts (248 μmol for TiO_2 and 125 μmol for Ti-SBA-15), one can see that considerable more sites are available than the amount of propene oxide that is observed. However, for the epoxidation, both gold and titanium sites are requirements. The number of Ti sites in the direct vicinity of a gold particle, assuming uniform spherical gold particles of 4 nm in size completely surrounded by Ti, is calculated to be 0.3 μmol, which is considerably lower. Possible explanations for the larger amount of $P^{16}O$ can be:

- Propene oxide adsorbs, after it is produced, reversibly at other sites of the catalyst, not in the vicinity of a gold particle. This assumption is supported by thermogravimetrical absorption experiments we published previously [6]. On P25 titania 1.5 wt% PO adsorbs at 323 K (corresponding to 78 μmol for 0.3 g catalyst), of which 0.1 wt% adsorbs reversibly (5.1 μmol). This latter amount is in good agreement with the size of the oxygen pool responsible for the propene oxide release observed in this work (7.9 μmol for the TiO_2 supported catalyst).
- The support provides oxygen for the epoxidation. This can only be the case for the Titania support, since for Ti-SBA-15 only Ti is reducible, not Si. The number of reducible sites for Ti-SBA-15 is therefore by far insufficient.
- A large number of smaller gold particles, which could not be observed by TEM must be present. Small gold particles are indeed reported to be highly active in the epoxidation [26]. A supporting indication for this assumption is the fact that in an EXAFS analysis of our catalysts [27] we consistently obtained smaller average gold particle sizes for EXAFS compared to those for TEM. For the Au/TiO_2 catalyst, this was 1.5 nm compared to 4 nm. However, a gold particle of 1.5 nm still consists of about 100 atoms, which means that the amount of (reaction) sites in the neighborhood of gold particles will still not be sufficient to have been the sites where the $P^{16}O$ was absorbed.

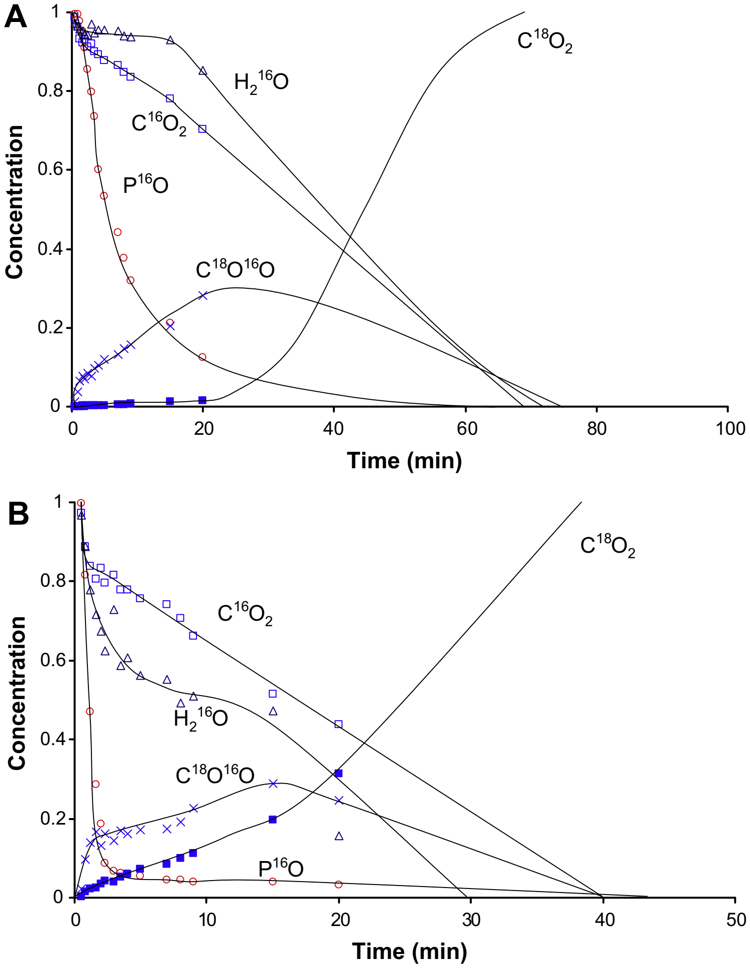


Fig. 6. Extrapolated SSITKA responses for the experiments shown in Figs. 2 and 5, used for the determination of the amounts of adsorbates on the catalysts. (A) Au/TiO_2 catalyst (Fig. 2); (B) Au/Ti-SBA-15 catalyst (Fig. 5).

The amount of $H_2{}^{16}O$ released from the catalysts after the switch to oxygen-18 (Table 2) needs different explanations for the two catalysts studied. For the titania-supported catalyst, this amount of water is almost 20 times larger than the total number of sites available for the adsorption of water (Table 3). The most likely explanation for this large amount of ^{16}O present in the water produced must therefore be that it is originating from the titania. It cannot be determined from these experiments, however, if the support oxygen ends up in the water when the water is produced, or if it is exchanging with the support afterwards (see Scheme 2). For Rutile-type titania, this isotopic exchange of oxygen in water with support oxygen in the titania has been confirmed experimentally [28]. A similar exchange can be expected for the P25 support (85% anatase, 15% rutile) used in this study. For the Ti-SBA-15-supported catalyst, the specific surface area is considerably higher. For this catalyst, the ^{16}O containing water leaving the reactor after the SSITKA switch could either have been adsorbed physically, or have been produced by an exchange with surface O or OH. Water is produced via two routes, partly a co-product in the epoxidation, and for the largest part as a product of the direct hydrogen oxidation producing water. Since the large amount of adsorbed water points to a physical adsorption over the entire support structure causing the delay in the isotopic transients, linking the isotopic transients for the propene oxide and water formation is not possible.

Table 1
Integrated areas for the isotopic composition of ^{16}O containing products after the isotopic switch in the SSITKA experiments.

	Au/TiO_2	Au/Ti-SBA-15	
Propene oxide ^{16}O	8.0	2.0	min
$C^{16}O^{18}O$	16[a]	7.5	min
$C^{16}O_2$	40	20	min
$H_2{}^{16}O$	700[a]	17	min

[a] The accuracy of these values is lower due to the extrapolation made (possible error estimated to be up to 50% of this value).

For CO_2 it could be seen from the SSITKA experiment shown in Fig. 4 that the delay in response of the signal is very small when a SSITKA transient if measured for a $^{12}CO_2$ to $^{13}CO_2$ switch, indicating a very minor physical adsorption. The slow transients for CO_2 in Figs. 2 and 5 are, therefore, more likely caused by a slow formation. It can also be observed that for the Ti-SBA-15 catalyst, the exchange of oxygen from CO_2 produced with the support is minor. If such an exchange would be occurring at a significant rate, it would not be possible that $C^{18}O_2$ would be present in a larger concentration as a product than $C^{16}O^{18}O$ while $C^{16}O_2$ is still the primary product. As a consequence, the isotopic composition of the CO_2 as it is observed in the experiments must be identical or at least close to the isotopic composition released from the sites where it is produced.

The quantity of ^{16}O containing carbon dioxide liberated from the catalysts after the SSITKA switch is quite large, especially for the Ti-SBA-15-supported catalyst. To explain this, one needs to consider that the CO_2 response due to adsorption on the catalyst is only

Table 2
Catalytic data for both gold catalysts and calculated amounts of adsorbate species using the catalytic data and the information provided in Table 1.

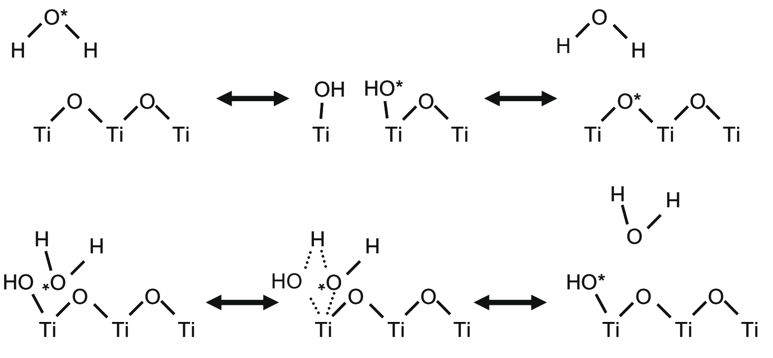
	Au/TiO_2	Au/Ti-SBA-15	
Temperature	323	423	K
Total flow rate	50	50	ml/min
Propene flow	5	5	ml/min
Propene flow	200	200	μmol/min
Conversion	0.5	1.5	%
Propene converted	1.0	3.0	μmol/min
PO selectivity	99	90	%
PO produced	1.0	2.7	μmol/min
CO_2 selectivity	1	10	%
CO_2 produced	0.03	0.9	μmol/min
Hydrogen efficiency	15	3	%
Water produced	6.6	90	μmol/min
PO adsorbed	**7.9**	**5.5**	μmol
CO_2 adsorbed-type 1 (precursor for $C^{18}O^{16}O$)	**0.48**	**7.1**	μmol
CO_2 adsorbed-type 2 (precursor for $C^{16}O_2$)	**2.4**	**36.0**	μmol
H_2O adsorbed	**4620**	**1540**	μmol

Table 3
Physical data on the gold catalysts and calculated numbers of adsorption sites available.

	Au/TiO_2	Au/Ti-SBA-15	
Weight in reactor	0.300	0.300	g
Surface area	50	490	m^2/g
Surface area	15	147	m^2
Si/Ti ratio	–	40	–
Ti content (as TiO_2)	–	3.2	wt%
Ti sites[a]		125	μmol
Ti sites[b]	16.6	–	μmol/m^2
Si sites[b]		13.6	μmol/m^2
Ti sites	248		μmol
Si sites		2000	μmol
Au loading	1	1	wt%
Au in reactor	3	3	mg
Au particle avg. size	4	4	nm
Au atoms	15.2	15.2	μmol
Au particles[c]	7.7	7.7	nmol
Ti neighbor sites	0.31	0.31[d]	μmol

[a] Ti is deposited by grafting, it is therefore assumed that all Ti is on the surface.
[b] Based on bulk density of anatase and quartz.
[c] Assuming spherical particles.
[d] Assuming that the Au particles only have Ti/O atoms as immediate neighbors. A circle perimeter equal to the particle diameter is taken for this site calculation.

delayed very little (Fig. 4), and that gold particles are responsible for the complete oxidation (no oxidation by the support itself) [6,20]. The 43 μmol of ^{16}O containing carbon dioxide that the Ti-SBA-15-supported catalyst produces after the SSITKA switch should, therefore, originate from reaction or adsorption sites near gold particles. The number of sites directly neighboring gold particles (taking the observed TEM particle size of 4 nm), however, is only in the order of 0.3 μmol. This value was calculated assuming spherical gold particles of 4 nm (the observed TEM particle size), with a 4 nm circular perimeter and assuming that all sites are Ti sites, in reality a large number will be Si. Haruta and Daté [29] stated that hemispherical particles are the active gold particles, but from our TEM micrographs we do not have indications that our gold particles are indeed hemispherical, so this assumption was not made in the calculations. However, even if hemispherical particles were assumed or a larger perimeter would be taken into account than only the directly adjoining Ti sites, the number of available oxygen atoms will be considerably smaller than 43 μmol. It would be possible that these sites would contain adsorbed ^{16}O containing intermediates and that an exchange with support oxygen would provide some more ^{16}O; however, since the Si of the support is not reducible and the amount of additional ^{16}O needed is quite significant, such an exchange is less likely to be a sufficient explanation. The most probable explanation is that apart from the visible 4 nm gold particles, also a large number of TEM invisible small gold particles are present, as is supported by our EXAFS data [27]. The TEM microscope used for the determination of the gold particle size has a lower detection limit for gold particles of approximately 1 nm in size. These EXAFS data, providing an averaged particle size for all gold atoms, indicate an average particle size of 1.0 nm. If one would hypothesize a bimodal distribution of 4 nm gold particles (TEM visible) and TEM invisible single gold atoms on the catalyst, one can calculate that about 1/3rd of the gold atoms would be present as single atoms on the catalyst (i.e. about 5 μmol), which will greatly increase the number of possible Ti neighboring sites and bring this more in agreement with the calculated number of adsorbates. Similar calculations can be done for small gold clusters. The catalytic activity of small 6–10 atom gold clusters was recently discussed by Ojeda and Iglesia [30] and



Scheme 2. Proposed mechanisms for exchange of oxygen in the water produced by the catalyst with oxygen from the support.

Lee et al. [31]. For example, if one would assume that the TEM 'invisible' gold would consist of 0.4 nm large 6 atom gold clusters [32], it can be calculated that about half of the gold present would be in the form of these 0.4 nm clusters (1.2 μmol). A larger amount of reaction sites on the catalyst for propene epoxidation and for complete combustion explained by the presence of a large amount of small gold particles/single gold atoms, is therefore a feasible explanation. The concept of TEM-invisible gold particles playing an important role in gold–titania based propene epoxidation catalysts was also proposed earlier by Delgass et al. [33] and Oyama et al. [34].

It can be argued that the calculated size of the oxygen pools for CO_2 and propene oxide in Table 2, which we linked to titanium sites neighboring gold, is underestimating the number of titanium sites. In Fig. 3 it can be seen that the catalyst is deactivating, and that initially even more active sites should have been present. The 'deactivation' in Fig. 3, however, is not a true deactivation in our opinion, but rather a strong adsorption of species, in particular carbonates. We previously modeled this catalytic behavior successfully [17]. In this modeling, we assumed the formation of carbonate species, which would very slowly desorb from the catalyst as carbon dioxide. This can explain the very slow carbon dioxide transients we observed in this work, and it implies that no sites are lost due to a catalyst deactivation, but rather that they are simply temporarily occupied by an adsorbate species, which is part of the observed oxygen pool in the SSITKA experiments.

A general remark needs to be made on the calculations of sites and adsorbate species that have been made. The catalysts used will almost certainly contain many different types of gold and titanium sites. In the calculations, we have lumped all these different sites together since we are not able to make a distinction between them from the experiments performed.

5. Conclusions

SSITKA experiments showed that the size of the oxygen pool on the catalyst surface is very high for both the Au/TiO_2 and the Au/Ti-SBA-15 catalysts. The species in this oxygen pool include reaction intermediates and products (adsorbed propene oxide, carbon dioxide, and water). Because of the manner in which the SSITKA experiments are performed, it can be concluded that these intermediates are not spectator species. The total amount of adsorbates that were estimated from the size of the corresponding oxygen pools is of the same order of magnitude as the estimated total amount of adsorption sites available on the catalysts, which indicates that product desorption is likely to be a rate limiting factor. This assumption is also supported by the slow isotopic transients that are observed. The main aim of this study was to determine if support oxygen plays a role in the formation of propene oxide. However, this question cannot be answered conclusively.

Carbon dioxide is produced via at least two different pathways: for one pathway the oxygen storage pool is very small, the other involves a much larger oxygen storage pool. The amount of ^{16}O containing propene oxide produced after the SSITKA isotopic switch is larger than the estimated number of sites at which it can be produced, which indicates that support oxygen is ending up in the product propene oxide; however, a strong but reversible propene oxide adsorption on the catalyst cannot be ruled out as an alternative explanation. Given the commonly accepted view that both the epoxidation and complete combustion only proceed near the gold particles on the support, the amount of ^{16}O containing propene oxide and carbon dioxide produced after the SSITKA switch indicates that the catalyst contains also a significant amount of sub-nanometer sized gold particles, providing additional reaction sites.

Water, which is produced in large quantities as a co-product, has a very large SSITKA retention amount, indicating a large originating oxygen pool. For the Ti-SBA-15-supported catalyst, this can be explained by water adsorption on the entire support, including on the Si–OH sites. For the Ti-supported catalysts, the adsorbed amount is considerably larger than the available surface area for adsorption of water. For this catalyst, support oxygen must be ending up in the water produced, which can either happen by a role of support oxygen in its formation, or by an exchange with the support afterwards. The involvement of support oxygen, either directly, or via an exchange afterwards, explains the very large oxygen pool for water. These very large oxygen pools also explain the very slow isotopic transients.

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