

Stability and Selectivity of Au/TiO₂ and Au/TiO₂/SiO₂ Catalysts in Propene Epoxidation: An *in Situ* FT-IR Study

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In situ FT-IR spectroscopy was used to study the surface species involved in the selective epoxidation of propene with an O₂/H₂ mixture over a deactivating 1 wt% Au/TiO₂ catalyst and a non-deactivating 1 wt% Au/TiO₂/SiO₂ catalyst. Propene adsorbs weakly on both catalysts via γ -hydrogen bonding with surface hydroxyl groups of the TiO₂ or TiO₂/SiO₂ support. Propene adsorption is completely reversible at temperatures between 300 and 400 K. Irreversible adsorption of propene oxide (PO) was observed on both catalysts, yielding bidentate propoxy moieties. Similar propoxy species are formed after prolonged exposure of the catalysts to a propene/oxygen/hydrogen mixture. Deactivation of TiO₂ catalysts is explained by the formation of these propoxy groups on Ti sites active and selective in propene epoxidation. Neighboring acidic Ti sites are involved in coupling of PO onto these sites. Occupation of selective sites with propoxy groups is limited on TiO₂/SiO₂ catalysts. On this support, propoxy groups are located on acidic agglomerated TiO_x sites and linked to an Si–OH functionality. These groups are not involved in the selective epoxidation of propene, which occurs over isolated tetrahedral sites.

Besides propoxy groups, surface compounds with absorptions in the C=O stretching range (acetone and propanal) were observed on both catalysts. Formate and acetate species (implying C–C bond cleavage) were identified exclusively on the Au/TiO₂ catalyst. The relevance of these species to the selectivity of the catalysts investigated is discussed. © 2001 Academic Press

Key Words: FT-IR; gold; titania, propene; propene oxide; epoxidation; deactivation; mechanism.

1. INTRODUCTION

Highly dispersed Au/TiO₂ catalysts recently received considerable attention, as these catalysts were found very active in low temperature CO oxidation (1). Furthermore, an extraordinary selectivity in the oxidation of propene to the corresponding epoxide was claimed (>99%), using a combination of H₂ and O₂ as oxidation mixture (2). Additional studies of the epoxidation reaction indicated several drawbacks of the Au/TiO₂ catalyst. First, the low conversion (1–2%) obtained under typical reaction conditions

(atmospheric pressure, 323–423 K) cannot be improved by increasing the reaction temperature, because this leads to extensive by-product formation. Secondly, the low efficiency of hydrogen (relatively large amounts of water are formed) is hard to prevent. Finally, significant deactivation of Au/TiO₂ catalysts within several hours on stream occurs.

Many aspects of Au/TiO₂-based catalysts are still not very well understood. A hydrogen peroxy species has been proposed as oxidant in the epoxidation reaction (3), but this is still speculative (4, 5). The mechanism of deactivation has not been investigated in much detail. Interestingly, deactivation of Au catalysts can be prevented by application of dispersed TiO₂ supports, like TiO₂/SiO₂ and titanium-silicalite-1 (TS-1) (3, 6). These catalysts usually show epoxidation activity at temperatures between 398 and 423 K, which is 50 K above the temperatures where Au/TiO₂ catalysts yield PO selectively. Nijhuis *et al.* (3) propose oligomerized propene oxide to be responsible for deactivation of Au/TiO₂, based on TG/DSC profiles.

Infrared studies on Au/TiO₂-based catalysts were mainly focused on the active gold species in low temperature CO oxidation, concerning the interaction of CO with Au particles (7, 8). The water gas shift reaction was also previously studied using *in situ* IR by Boccuzzi (9). The interaction of propene, propene oxide, and a reaction mixture of H₂, O₂, and propene with Au/TiO₂-based catalysts has not been investigated previously using IR spectroscopy, although PO has been used as a probe molecule to characterize catalyst acidity by infrared analysis (10). In this paper IR spectra of reactants (propene, hydrogen, and oxygen) and propene oxide, interacting with deactivating Au/TiO₂, and nondeactivating Au/TiO₂/SiO₂ catalysts, are presented. Several aspects of the deactivation mechanism, as well as the selectivity of the Au/TiO₂ and Au/TiO₂/SiO₂ catalysts, are discussed.

2. CATALYSTS AND METHODS

A 1.6 wt% TiO₂ (0.1 monolayer) TiO₂/SiO₂ support was prepared by reaction of titanium(IV)ethoxide (Fluka, 97%) in 2-propanol with surface hydroxyls of SiO₂ (Aldrich

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Davisil 646) based on a method by Rajadhyaksha and co-workers (11). TiO_2 (P25, Degussa) was used as received. Catalysts containing 1 wt% Au were prepared by deposition precipitation of $\text{Au}(\text{OH})_3$, by slowly adding a AuCl_3 (Fluka) solution to a suspension of the support at pH 10 (3). All catalysts were thoroughly washed before calcination at 673 K to prevent chlorine contamination. TEM analysis showed the formation of Au metal particles in the 3–6 nm range for both supports. Diffuse reflectance UV-Vis spectroscopy confirmed that the $\text{TiO}_2/\text{SiO}_2$ support did not contain anatase (only a band of isolated tetrahedral Ti at 230 nm was observed), indicating a high dispersion of Ti species.

The FT-IR measurements were performed using an *in situ* IR cell with CaF_2 windows. This cell was designed and built at the University of Amsterdam (12). Gas could be fed to the cell using a 4-way valve (Valco), which was configured to select two separate gas feeds. Using a flow of 30 ml/min, the cell was completely refreshed in about 30 s after the valve was switched. The samples were prepared in the form of self-supporting wafers ($\sim 20 \text{ mg/cm}^2$) at pressures of 3–4 ton/cm². Pretreatment of the wafers consisted of drying at 398 K in He. Spectra were recorded using a Nicolet Magna IR 860 spectrometer equipped with an MCT detector. Unless stated otherwise, spectra were recorded against a background of the sample at the reaction temperature under He at 4 cm⁻¹ resolution, using coaddition of 64 scans.

Gases applied (propene, 1.5% PO in He, H_2 , O_2 , and He) were of HP or UHP grade and dried before use. The IR measurements were performed using a 10% propene in He mixture, 1.5% PO in He mixture, and a mixture of 10/10/10/70 vol% of propene, O_2 , H_2 , and N_2 , respectively. Reference (alcoholic) compounds were fed to the *in situ* cell by saturation of N_2 with the required solvent in a 10-ml glass saturator at room temperature, followed by addition of dry N_2 , leading to a 10 times dilution of the concentration of the reference compound. *In situ* reactivity studies were performed at temperatures ranging from 348 to 423 K.

3. RESULTS

3.1. Catalysts

Spectra of the Au/TiO_2 and $\text{Au}/\text{TiO}_2/\text{SiO}_2$ catalysts using the empty cell as reference are shown in Fig. 1. The hydrocarbon signals in the catalysts are of only low intensity (Fig. 1b), suggesting that little contamination was present after the preparation procedures and calcination at 673 K. This is in agreement with several observations in the literature (13, 14). The IR spectra of TiO_2 (not shown) and Au/TiO_2 are quite similar and comparable to the spectra recently published by Martra (15). The spectra presented in the following paragraphs were recorded using the spectra

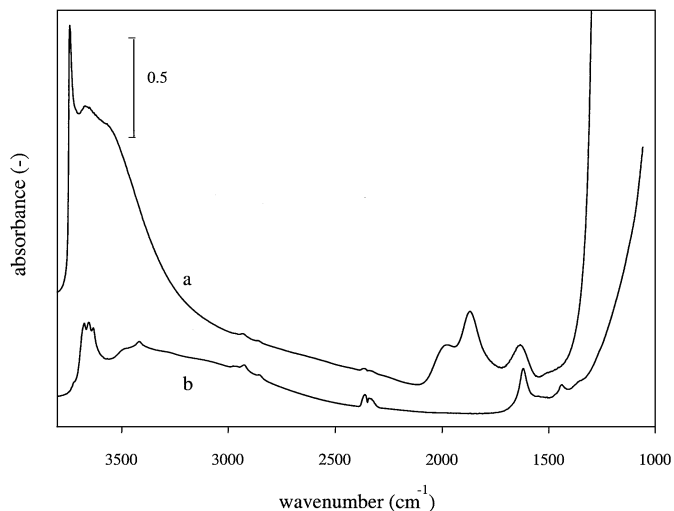


FIG. 1. IR spectra of (a) $\text{Au}/\text{TiO}_2/\text{SiO}_2$ (398 K, in He) and (b) Au/TiO_2 (348 K, in He) catalysts.

shown in Fig. 1 as a background. Hence, the interactions of various molecules were studied on catalysts calcined at 673 K in the preparation procedure, and dried in He at 398 K in the IR cell.

3.2. Adsorption of Propene

Changes in the hydroxyl stretching region of the Au/TiO_2 catalyst upon propene adsorption at 300 K are shown in Fig. 2 (top spectrum). The intensity of the hydroxylic vibrations is clearly affected by the presence of gas-phase

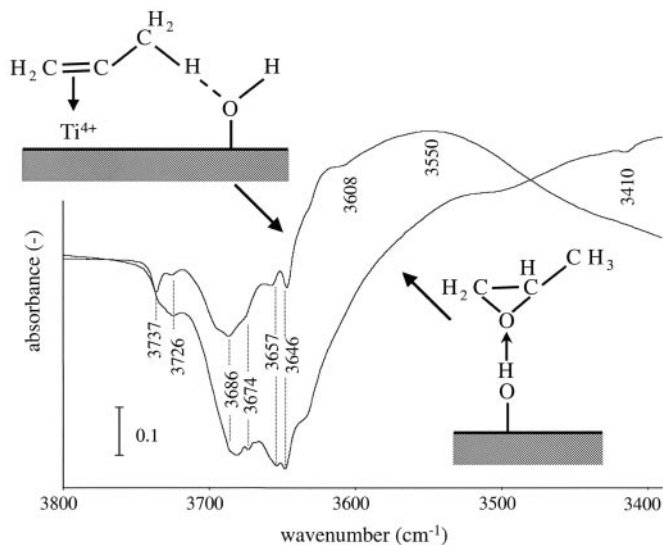


FIG. 2. Changes in the OH stretch region upon interaction of respectively propene (top spectrum) and propene oxide (PO) (bottom spectrum) at 323 K with Au/TiO_2 . Proposed absorption complexes are given in the inset.

propene. Since the spectrum of Au/TiO₂ was used as background, decreasing intensities show as negative bands. Ti–OH stretching bands are located at 3737, 3726, 3686, 3674, 3657, 3646, and 3608 cm⁻¹. Spectroscopic identification of the OH groups of various TiO₂ morphologies has been extensively discussed (13–20). Our (negative) spectrum corresponds to spectra presented by Tanaka and White (13), although various bands are shifted to slightly higher wavenumbers. The 3737 cm⁻¹ band is probably due to a silica impurity (18, 20). The presence of about 0.25 wt% SiO₂ in the P25 TiO₂ sample was confirmed by XRF analysis. The 3686 cm⁻¹ band contains contributions at lower (at 3674 cm⁻¹), as well as higher frequencies. The 3726 and the shouldered 3686 cm⁻¹ bands have previously been assigned to the isolated OH groups of rutile and anatase, respectively (16, 17). The P25 TiO₂ support consists of about 80 wt% anatase and 20 wt% rutile (21). The bands at 3657, and 3646, and 3608 cm⁻¹ have been assigned to hydrogen bonded OH groups, as well as water molecules adsorbed on different crystal phases (16, 19, 22). Intensity differences between literature spectra and our (negative) spectrum are likely related to the relative contribution of the hydroxyl groups to the interaction with propene. Besides the negative bands, a broad positive band is developed upon propene adsorption, centered around 3550 cm⁻¹, which can be assigned to H-bonded OH groups. Adsorption of ethene and propene on TiO₂ has been studied by Davydov *et al.* (23). These authors showed that ethene adsorption did not result in decreasing Ti–OH intensities. This suggests that hydrogen interactions occur via the methyl group of propene, as illustrated in Fig. 2. It should be noted that the 1635 cm⁻¹ band of adsorbed propene was hard to identify in our spectra, since the O–H bending deformation of physisorbed water is in close proximity to this band, located around 1620 cm⁻¹.

Upon propene adsorption, the spectrum of the Au/TiO₂/SiO₂ catalyst (not shown) is dominated by a negative band at around 3737 cm⁻¹, which is assigned to silanol groups of the silica support. In the Ti–OH region, only a weak negative band at 3716 cm⁻¹ is present, assigned to an isolated Ti–OH group (16, 24). Isolated Ti species were also identified by DR-UV-Vis analysis of these catalyst samples (3, 6).

The interaction of propene with both catalysts is completely reversible: after removal of gas-phase propene the spectra in the OH region were rapidly restored (the negative and positive bands disappeared), and adsorbed species did not remain on the surface. Furthermore, at temperatures above 473 K interactions of propene with the Ti–OH and Si–OH groups were no longer observed.

3.3. Adsorption of Propene Oxide–Au/TiO₂

The changes in the OH spectral region of Au/TiO₂ upon propene oxide adsorption are also presented in Fig. 2. Com-

pared to the adsorption of propene several differences can be identified:

(i) The acidic (lower wavenumber) OH groups have a relatively stronger interaction with PO than with propene. The OH vibrations located at 3657 and 3646 cm⁻¹ are more affected. Introduction of PO also leads to a decrease of the OH stretching vibration located at 3410 cm⁻¹, which was not observed upon propene adsorption. This band has been assigned both to H-bonded hydroxyls of the rutile phase (16) and isolated OH, bridged between two adjacent Ti moieties (17). The latter assignment seems more likely, as H-bonded hydroxyls would give rise to broader bands.

(ii) The maximum of the broad positive band is located at 3320 cm⁻¹ (not shown) upon PO adsorption, which is at a significantly lower wavenumber than observed after propene adsorption (3550 cm⁻¹). This larger shift in OH-group frequencies indicates that the hydrogen bonds formed upon interaction with PO are stronger compared to propene adsorption (22).

(iii) Removal of gas-phase PO does not restore the original spectrum; the broad feature at 3320 cm⁻¹ disappears, suggesting reversible adsorption, but the negative OH absorption bands hardly change. This suggests that a chemical transformation of the OH groups by irreversible PO adsorption also occurs.

The C–H stretching and bending regions of the adsorbed species are shown in Figs. 3A and 3B, respectively. In the presence of PO, absorptions at 3049, 3001, 2970, 2931, and 2870 cm⁻¹ can be identified in the C–H stretching region. The 2870 cm⁻¹ has two shoulders on the low- and high-frequency side (at around 2855 and 2880 cm⁻¹, respectively). Changing the gas-phase composition to He results in desorption and decomposition of adsorbed PO, as indicated by the decreasing 3049 cm⁻¹ band (which is related to the CH₂ stretch of the methylene group), and the decreasing intensity of the 3005 cm⁻¹ band, which is assigned to the methine C–H stretching vibration of the PO molecule. The decreasing band at 1270 cm⁻¹ (Fig. 3B) is indicative for the symmetrical ring breathing mode of adsorbed PO (25). Additional decreasing bands of adsorbed PO are located in the C–H bending region (1550 to 1300 cm⁻¹) at 1486, 1445, and 1410 cm⁻¹ (CH₂ and CH₃ bending and deformation modes).

Weak C=O stretching vibrations can be observed in the spectra at 1660, 1690 (sh), and 1730 cm⁻¹ (Fig. 3B), suggesting that some adsorbed PO is converted to an oxidized, C=O containing surface species. This might be an adsorbed ketone (acetone (26)) or aldehyde (propanal). The 1660 cm⁻¹ band is decreasing as a function of reaction time in He, while the 1730 cm⁻¹ vibration and a shoulder at 1690 cm⁻¹ are not affected.

The remaining C–H stretching vibrations of the adsorbed species formed by transformation of adsorbed PO can be assigned to CH₃ and CH₂ (as)symmetric stretch vibrations.

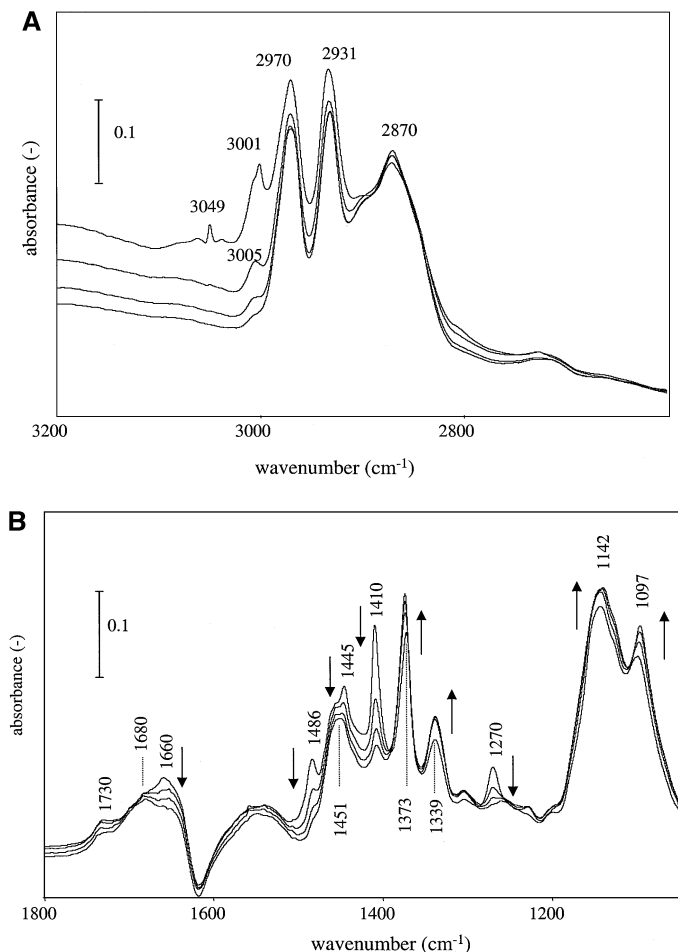


FIG. 3. (A) Adsorption and desorption of propene oxide (PO) from the Au/TiO₂ catalyst at 323 K by flushing in He. Top to bottom: in 1.5% PO in He, in He after respectively 3, 10, and 25 min. Region: 2600–3200 cm⁻¹. (B) Adsorption and desorption of PO from the Au/TiO₂ catalyst at 323 K by flushing in He. Top to bottom: in 1.5% PO in He, in He after respectively 3, 10, and 25 min. Region: 1050–1800 cm⁻¹.

The band at 1451 cm⁻¹ can be assigned to $\delta_{as}(\text{CH}_3)$, and the 1373 and 1339 cm⁻¹ bands to $\delta_s(\text{CH}_3)$ and $\delta_s(\text{CH})$, respectively (27). Strong bands are also located at 1142 (which is mainly the C–O–Ti stretch vibration) and at 1097 cm⁻¹ (C–C stretch) (28).

The spectral characteristics of the adsorption, desorption, and decomposition of PO are independent on the presence of gold or the amount of adsorbed water on the catalyst. This was verified by studying the interaction of PO with a TiO₂ P25 support only, and by recording reference spectra of a catalyst that was not dried at 398 K in He before use. These samples show the same bands in the IR spectra.

The spectral characteristics indicate that besides a minor amount of species containing a C=O functionality, a large fraction of the adsorbed epoxide is converted to another irreversibly adsorbed species. Adsorbed (intact) PO

is probably H-bonded to acidic OH groups as given in the insert of Fig. 2. Therefore, it is likely that the irreversible adsorbed species are formed via acid-catalyzed opening of the epoxide ring, yielding a mono dentate (*i*, or *n*-propoxy), or bidentate propoxy species. To further validate the assignment, the adsorption of *i*-propanol, *n*-propanol, and 1,2-propane diol on Au/TiO₂ was studied at 348 K. These spectra are compared with the spectrum of the catalyst after PO adsorption at 348 K in Fig. 4. Unfortunately, the type of species formed by interaction of the alcohols with the catalyst appears quite different from the species formed upon PO adsorption. Spectra of the adsorbed alcohols, and especially of 1,2 propane diol, contain a large C=O band at 1695 cm⁻¹. This indicates conversion of the alcohols over the Au/TiO₂ catalyst to acetone. The assignment to the ketone is evidenced by the fact that no CH stretch of an aldehyde (HCO) at about 2740 cm⁻¹ is observed (10), while the aldehyde C=O stretching vibration is also expected at lower wavenumbers (25). The diol does not form propoxy linkages, which is in agreement with the extensive acetone formation. On the other hand, the spectra of *n*- and *i*-propanol contain bands in the 1500 to 1150 cm⁻¹ region that are indicative of the corresponding adsorbed propoxy product. The observed frequencies of adsorbed *i*-propanol on Au/TiO₂ are in good agreement with literature data of adsorbed *i*-propanol on TiO₂ (27, 29) and the Ti–(O–CH₂(CH₃)₂)₄ complex (30). The spectra of the adsorbed *n*- and *i*-propanol show profound differences in the $\nu(\text{C–O})$ and $\nu(\text{C–C})$ region (1050–1200 cm⁻¹), mainly related to different C–C stretching frequencies. In this region the PO spectrum resembles that of *n*-propanol, but the spectra are significantly different in the C–H stretching region. Concluding, the spectrum of

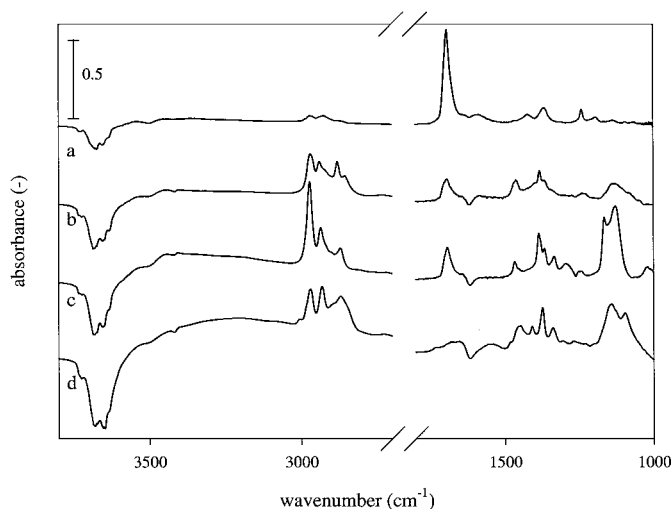


FIG. 4. Comparison of spectra after adsorption of (a) 1,2-propane diol, (b) *n*-propanol, (c) *i*-propanol, and (d) PO on the Au/TiO₂ catalyst at 348 K.

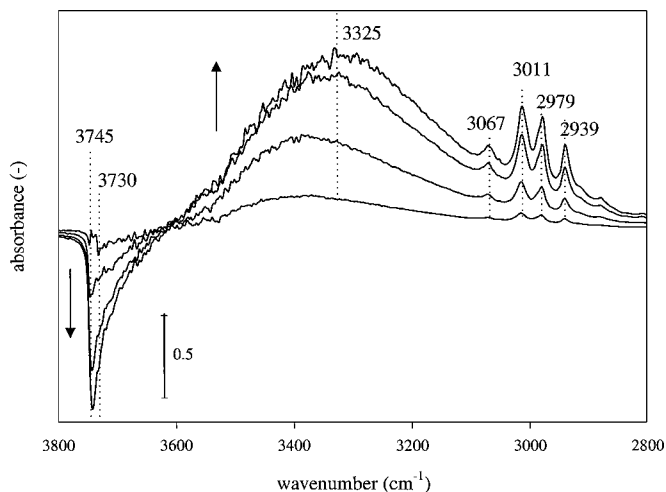


FIG. 5. Time-dependent spectra taken upon introduction of PO to the IR cell, containing Au/TiO₂/SiO₂ catalyst at 323 K (after 30, 60, 90, and 120 s, respectively).

adsorbed PO does not unambiguously correspond to that of one of the adsorbed alcohols. It appears most likely that a bidentate propoxy species is formed, although the presence of some monodentate propoxy species cannot be excluded.

3.4. Adsorption of Propene Oxide–Au/TiO₂/SiO₂

In Fig. 5 the changes in the spectrum of the Au/TiO₂/SiO₂ catalyst upon introduction of PO in the *in situ* cell are shown. Both the Si–OH (3745 cm⁻¹) and a Ti–OH group located at 3730 cm⁻¹ participate in the reactive adsorption of PO. The Ti–OH seems to decrease before the silanol absorption is affected (after 30 s), but after 60 s the spectrum is dominated by the Si–OH vibration. The intensity of the C–H stretching vibrations increases, due to the increasing PO concentration in the *in situ* cell. The desorption and decomposition of adsorbed PO are shown in Fig. 6A (broad adsorption at 3325 cm⁻¹ and the CH stretch frequencies) and Fig. 6B (CH bending vibrations). Upon desorption of PO, the intensity of the Si–OH and Ti–OH frequencies at 3745 and 3715 cm⁻¹, respectively, are partially restored (become less negative), in agreement with the decreasing 3325 cm⁻¹ band. Apparently a significant fraction of PO is reversibly adsorbed on the Au/TiO₂/SiO₂ catalyst. The signals at 3067 and 3011 cm⁻¹ are indicative of adsorbed PO. After desorption and transformation of adsorbed PO (decreasing bands at 3067, 3011 (Fig. 6A), and 1495, 1462, 1450, 1410, and 1374 cm⁻¹ (Fig. 6B)), the remaining adsorbed species gives rise to C–H bands at 2979 ($\nu_{as}CH_3$) and 2939 cm⁻¹ ($\nu_{as}CH_2$), with a shoulder of the symmetric methyl stretching at 2883 cm⁻¹. The remaining bands at 1460 and 1382 cm⁻¹ can be assigned to $\delta_{as}(CH_3)$, and $\delta(CH_3)$, respectively (27). As was previously discussed for the Au/TiO₂ catalyst, the spectral changes are related to the formation of propoxy species. Characteristic absorptions of

the propoxy compounds in the 1200 to 1100 cm⁻¹ region could not be analyzed for the Au/TiO₂/SiO₂ catalyst, due to the opacity of the sample in this spectral region. The C–H stretching vibrations are in excellent agreement with those observed in the spectrum of 1,2-propane diol adsorbed on the SiO₂ support (Fig. 7c). The diol mainly yields the bidentate propoxy species. Only a small fraction of the diol was converted to acetone. The different behavior of the diol on TiO₂ and TiO₂/SiO₂ suggests that dehydration and ketone formation are favored on TiO₂, while alkoxy formation is favored on TiO₂/SiO₂. On the other hand, formation of alkoxy species does not occur when silica is exposed to ethene oxide (EO) (31) or PO (10), which was confirmed by experiments with the Davisil SiO₂ support (not shown).

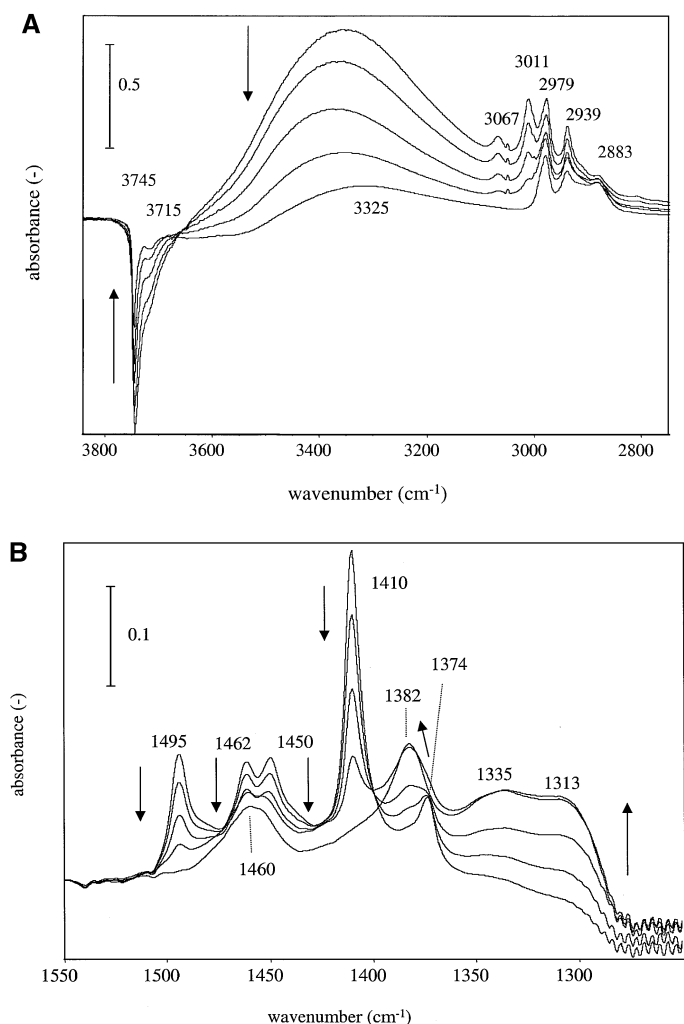


FIG. 6. (A) The interaction of PO (1.5% in He) with the Au/TiO₂/SiO₂ catalyst at different temperatures. Top to bottom: in PO at 323, 353, 378, and 400 K, in He at 400 K. Spectral region 2500 to 4000 cm⁻¹. (B) The interaction of PO (1.5% in He) with the Au/TiO₂/SiO₂ catalyst at different temperatures. Top to bottom (1410 band): in PO at 323, 353, 378, and 400 K, in He at 400 K. Spectral region 1200 to 1550 cm⁻¹.

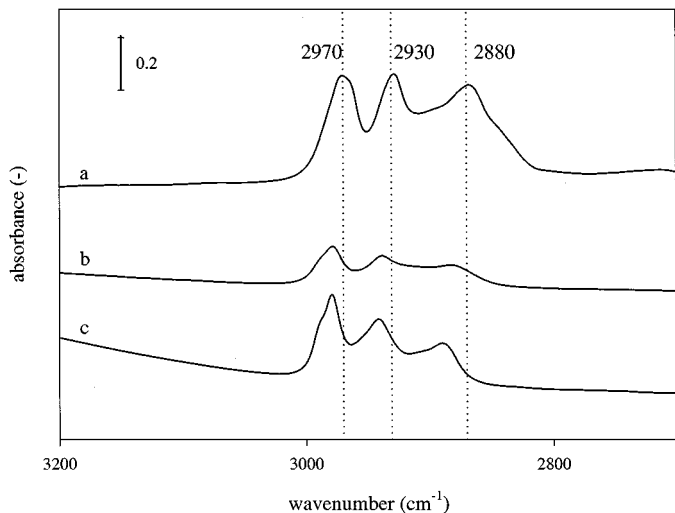


FIG. 7. Comparison of spectra recorded at 348 K (a) PO on Au/TiO₂, (b) PO on Au/TiO₂/SiO₂, and (c) 1,2-propane diol on SiO₂.

For temperatures between 348 and 423 K, PO was found to adsorb reversibly via H bonding with the Si–OH group located at 3745 cm⁻¹. This suggests that acidic Ti sites of the Au/TiO₂/SiO₂ catalyst are involved in the formation of the bidentate propoxy species. Activation of the PO molecule by Ti rather than Si is also in agreement with the spectra shown in Fig. 5, where first the Ti–OH band at 3730 cm⁻¹ and then the Si–OH band at 3745 cm⁻¹ respond to PO adsorption.

3.5. In Situ Reaction

To further investigate which surface species causes deactivation of the Au/TiO₂ catalyst, this catalyst and

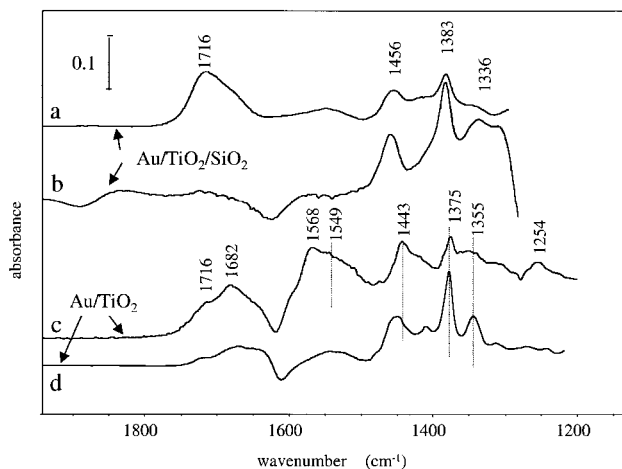


FIG. 8. Spectra of Au/TiO₂/SiO₂ and Au/TiO₂ catalysts. (a) Au/TiO₂/SiO₂ (H₂/O₂/propene mixture, 30 min, 373 K), (b) Au/TiO₂/SiO₂ (PO adsorption and decomposition, He, 5 min, 400 K), (c) Au/TiO₂ (H₂/O₂/propene 150 min, 373 K), and (d) Au/TiO₂ (PO adsorption and decomposition, He, 323 K).

Au/TiO₂/SiO₂ were exposed to the reaction mixture. The resulting spectra are presented in Fig. 8 and compared with those obtained after decomposition of adsorbed PO.

Obviously, the adsorbed species after reaction are quite similar in nature to the ones obtained after adsorption and decomposition of PO. The catalysts apparently convert the reaction mixture to PO, which is strongly adsorbed on the surface of both catalysts, yielding the bidentate propoxy species. It should be noted that interaction of the reaction mixture with the supports in the absence of Au did not show any propoxy group formation. Furthermore, in the presence of propene and O₂ only, no adsorbed species were found at the reaction temperatures studied. This suggests that the H₂/O₂ mixture yields a stronger oxidizing species over Au, than O₂ alone. The frequencies of the bidentate propoxy species show some intensity differences, explained by different reaction times and temperatures. The chemical interaction of PO with Au/TiO₂ was obtained at 323 K, while a temperature of 400 K was applied to establish interaction with the Au/TiO₂/SiO₂ catalyst. Specific absorption frequencies are located at slightly higher wavenumbers for the Au/TiO₂/SiO₂ catalyst, compared to the Au/TiO₂ catalyst (e.g., the 1443 band is shifted to 1456 cm⁻¹), in agreement with the spectra of adsorbed (and decomposed) PO. This suggests a somewhat different interaction of the propoxy species with the two catalysts. Furthermore, after exposure to the reaction mixture a band at 1682 cm⁻¹ can be observed in the spectrum of the Au/TiO₂ catalyst, while the C=O band is more pronounced and located at 1716 cm⁻¹ in the Au/TiO₂/SiO₂ spectra. These bands are assigned to adsorbed acetone and/or propanal. Based on spectra of propanal adsorbed on SiO₂ (not shown), it appears likely that the 1716 cm⁻¹ band has a predominant contribution of adsorbed (hydrogen-bonded) propanal, while the 1682 cm⁻¹ band of Au/TiO₂ is most likely related to adsorbed acetone, as previously discussed.

For Au/TiO₂, strong additional bands are located at 1570, and 1540 cm⁻¹, which are absent in the Au/TiO₂/SiO₂ spectra. These bands are in good agreement with the absorption frequencies of formate and acetate species. Oxidation of the bidentate complex apparently leads to acetate and formate species (thus implying C–C bond breaking). Contrary to Au/TiO₂, exposure of the propoxylated Au/TiO₂/SiO₂ catalyst to (hydrogen and) oxygen did not change the spectra, which indicates that the bidentate propoxy species on Au/TiO₂/SiO₂ are stable under oxidizing conditions.

4. DISCUSSION

4.1. Deactivation of Au/TiO₂ Catalysts

When the high selectivity of Au/TiO₂ catalysts in the oxidation of propene to PO was first discovered, deactivation of the catalyst was not considered (2). In more recent studies (3, 5) deactivation of the Au/TiO₂ was observed within

the first hours of operation. Surprisingly, when TiO_2 was supported on SiO_2 or other modified supports, deactivation occurred to a much less extent (3). Stangland *et al.* recently observed that deactivation was also less severe at relatively high temperatures (473 K), suggesting that a strongly adsorbed species causes deactivation (5). In this study the adsorption of both propene and propene oxide was studied to elucidate which compound was the precursor of the deactivating species.

In the absence of an oxidizing species, the adsorption of propene is reversible on both catalysts between 300 and 473 K. Above 473 K no adsorption could be observed. As no irreversible species are found it is very probable that deactivation of the Au/TiO_2 catalysts is not due to irreversible nonoxidative interactions of propene with the catalyst.

The interaction of PO on the Au/TiO_2 catalyst showed both reversible and irreversible adsorption. Interaction of PO with the acidic OH groups (see the insert of Fig. 2) results in the acid-catalyzed epoxide ring opening to form a propoxy species. Based on comparison of the spectrum of the PO decomposition product with spectra of adsorbed alcohols, the formation of a bidentate propoxy species is proposed. This interpretation is also supported by a study of Cant and co-workers (31), who studied ethene oxide adsorption in the presence of oxygen on Ag/TiO_2 catalysts at 493 K. These authors concluded that ethene oxide reacts instantaneously with surface hydroxyl groups to form glycol-like species. The experiments were very illustrative showing only two C-H stretching frequencies at 2930 and 2880 cm^{-1} , indicating that ethoxy groups were not formed (absence of the CH_3 vibrations at 2980 cm^{-1}). These spectral features also ruled out the formation of adsorbed

polymeric species, since they would give rise to only one C-H stretching frequency (31). PO oligomerization was suggested as the cause of deactivation by Nijhuis and co-workers (3). Dimerization of PO to the corresponding dioxane was observed (3). However, the spectra presented in this study did not show the characteristic C-O-C vibration of the dioxane compound (at 1260 cm^{-1}), in agreement with the results of Cant (31). The formation of the dimethyl dioxane compound may only occur at the higher partial pressures used by Nijhuis (34 kPa compared to 1.5 kPa of PO in this study). The presence of minor amounts of these compounds on the surface cannot be ruled out, but oligomeric or polymeric species appear not very likely to be responsible for catalyst deactivation.

The spectral observations and the different behavior of both catalysts with respect to deactivation are proposed to be explained by the chemical transformations schematically illustrated in Fig. 9. On Au/TiO_2 , interaction of PO with an acidic OH group results in the acid-catalyzed epoxide ring opening to form a monodentate propoxy species. It is proposed that the formed alcohol intermediate rapidly reacts with a neighboring selective Ti-OH epoxidation site, forming structure A. The facile acetone formation upon exposure of the TiO_2 support to 1,2-propane diol might be related to the initial presence of 2 OH groups in this molecule, and apparently reduces propoxy formation. To explain the stability in the epoxidation reaction of the $\text{Au/TiO}_2/\text{SiO}_2$ catalyst (3), it must be assumed that active Ti-OH epoxidation sites are not affected by the adsorbed bidentate propoxy groups. It is therefore proposed that the intermediate alcohol reacts with a neighboring Si-OH group

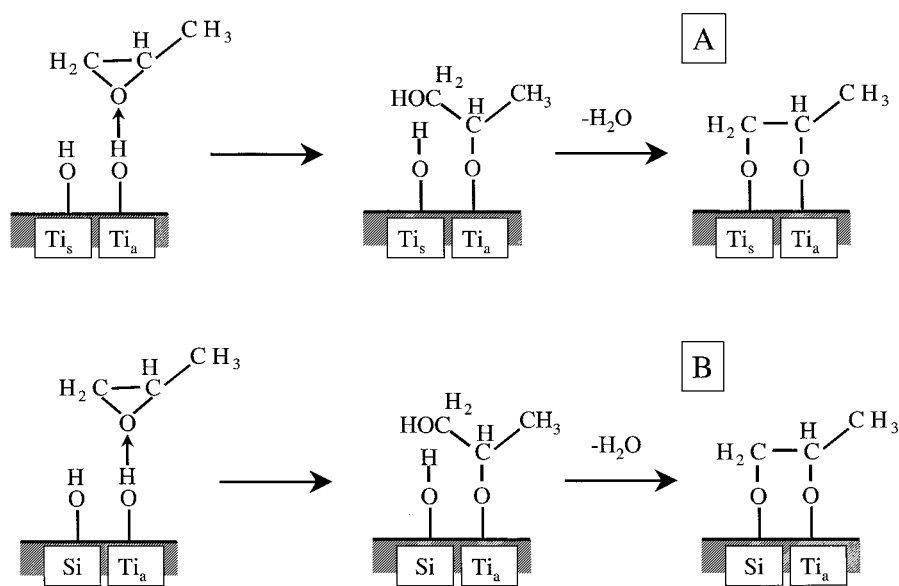


FIG. 9. Formation of bidentate propoxy species over the $\text{TiO}_2/\text{SiO}_2$ and TiO_2 support. Ti_s , selective epoxidation site; Ti_a , acidic PO coupling site.

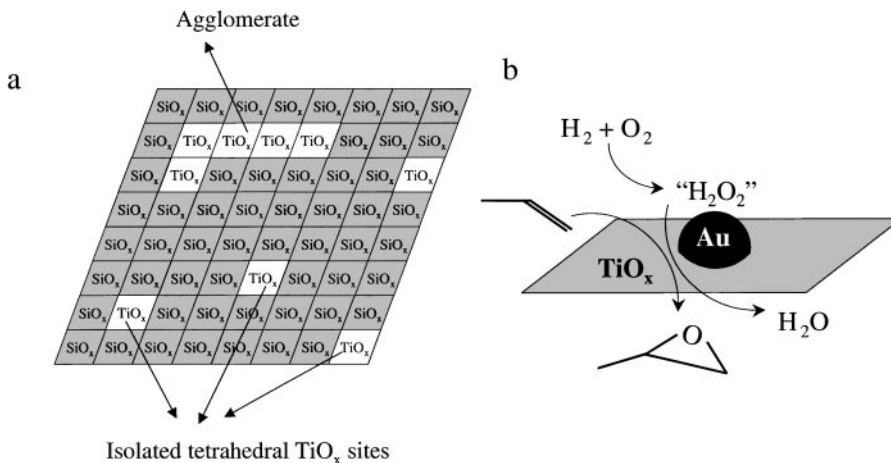


FIG. 10. Schematic representation of (a) TiO₂/SiO₂ support, including agglomerates and isolated sites. (b) Propene epoxidation mechanism over gold catalysts. Gold generates active oxygen species to epoxidize propene over Ti site.

(structure B). This is in agreement with the slightly different absorption frequencies observed in the spectra of both catalysts (Fig. 8). Apparently, due to the absence of neighboring acidic PO coupling sites (Ti–OH), the epoxidation sites of the Au/TiO₂/SiO₂ catalyst remain active. It should be noted that the Si–OH group itself is not reactive toward ring opening of PO. In the initial stage of PO adsorption (Fig. 5) a Ti–OH group reacts before the Si–OH group frequencies are changed. Furthermore, it has been reported that formation of alkoxy species does not occur when silica is exposed to EO (31) or PO (10).

To further discuss the role of specific TiO_x sites in the epoxidation reaction, Fig. 10 schematically shows the surface composition of the Au/TiO₂/SiO₂ catalyst. As was recently discussed by Gao and Wachs (32), two types of Ti species are usually present on supported TiO₂ systems; segregated oligomeric domains, and isolated Ti species (Fig. 10). The degree of homogeneity is associated with the relative amount of Ti–O–Si linkages in TiO₂/SiO₂ mixed oxides. Isolated tetrahedral sites (TiO₄) have been postulated as the active centers for the epoxidation of olefins by organic peroxides. This suggests that on Au/TiO₂/SiO₂ catalysts only agglomerates of TiO_x on SiO₂ are involved in the propoxy formation, while isolated tetrahedral epoxidation sites are not, as schematically indicated in Fig. 10. This is in excellent agreement with the acidity of the specific TiO sites. It has been stated that Brønsted acidity is associated with Ti–O–Si bridges where Ti atoms reside *not* in tetrahedral sites, but in pentahedral or octahedral sites (32) of agglomerated TiO_x moieties. These sites induce reaction of PO to propoxy groups on the TiO₂/SiO₂ surface, while on SiO₂ this does not occur. Whether unsupported TiO₂-specific sites (Ti–OH groups) are involved in the epoxidation reaction, or whether the reaction principally occurs on all Ti sites, could not be resolved from the spectra presented

in this paper. It is obvious from our spectra and reaction data, however, that on TiO₂ all Ti–OH groups, including the epoxidation centers, are involved in the formation of propoxy groups, explaining deactivation. At longer reaction times than applied in this study, and in the presence of higher concentrations of PO, propoxy groups might form oligomerized species which contribute to deactivation.

The location of Au in the catalysts and the role of the Au particles in the oxidation mechanism are not clear. Proximity of the Au particles to the isolated TiO_x epoxidation centers seems likely, since the postulate of the formation of hydrogen-peroxide intermediates, followed by interaction with the propene molecule is yet the most accepted reaction pathway. This intermediate is formed by Au activation of H₂ and O₂ (H₂O₂), as illustrated in Fig. 10. The deactivation of the catalysts is not likely to be related to the Au particles, since H₂O formation is not deteriorating as a function of time on stream (3). Au particles are neither likely to affect the formation of propoxy groups, since these are formed by interaction of PO with the TiO₂ or TiO₂/SiO₂ surfaces, as revealed by the various spectra presented in this paper.

Concluding, it is proposed that deactivation of Au/TiO₂ catalysts is due to the formation of propoxy species over (Brønsted) acid sites, blocking selective epoxidation sites on the TiO₂ surface. On the Au/TiO₂/SiO₂ catalysts, the epoxidation reaction probably occurs over isolated TiO_x sites, which are not involved in propoxy formation.

4.2. Activity and Selectivity of Au/TiO₂-Based Catalysts

The unique behavior of Au-based propene epoxidation catalysts is the excellent selectivity (usually reported to be above 99%). The IR spectra presented in this paper show, however, that bidentate propoxy groups and other products containing C=O entities are present on the surface of

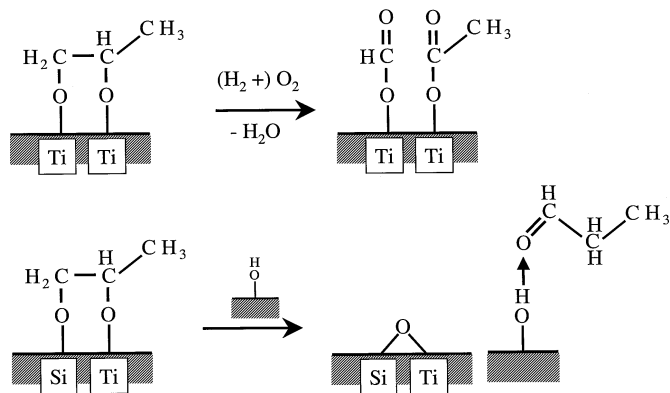


FIG. 11. Proposed formation of acetate and formate from bidentate propoxy species over TiO₂ and propanal formation over the TiO₂/SiO₂ support.

both catalysts. As indicated in Fig. 11, the bidentate propoxy species is oxidized to formate and acetate species upon exposure to oxygen on TiO₂, while the bidentate propoxy species on Au/TiO₂/SiO₂ could not be oxidized by prolonged exposure to oxygen or a hydrogen/oxygen mixture. Apparently, the Si–O–C bond increases the stability of the adsorbed molecule toward oxidation.

The discrepancy between the gas phase and surface product distribution can be explained by the assumption that the surface species are only formed in the initial stages of the reaction, and act as nonreactive spectator species during the subsequent course of the reaction. However, it should also be considered that products of PO decomposition can be present in the gas phase in too low amounts to be detected.

Principally, formates and acetates observed on the Au/TiO₂ catalyst are precursors for the formation of CO₂. Formation of ethanal and CO₂ from PO with H₂ and O₂ has been observed by Stangland and co-workers (5). Also the bidentate propoxy compound might be converted to propanal and acetone. For the Au/TiO₂/SiO₂ catalyst the main C=O band is in good agreement with hydrogen-bonded propanal, which is formed under inert atmosphere. Formation of propanal from PO has been observed by Piers and Rochester (33). These authors found that PO dissolved in CCl₄ reacts to propanal in minor amounts over aerosil SiO₂ at room temperature. This isomerization activity might be attributed to an increased acidity of the silanol groups induced by CCl₄. This is supported by a Si–OH band shift from 3740 to 3687 cm⁻¹ in the IR spectra of Piers and Rochester (33). For Au/TiO₂/SiO₂ it is tentatively proposed that reaction of the propoxy species to propanal involves recombination of Si–O and Ti–O to Si–O–Ti, as given in Fig. 11.

By-products, like ethanal, CO₂, acetone, and propanal, have been observed in the gas phase at higher temperatures (2, 3), but (precursors) seem to be present at reaction temperatures which appear to induce high selectivity.

Industrial application of Au catalysts will be complicated if the PO product must be separated from a stream containing oxygenates such as propanal, acetone, and ethanal. Dow Chemical has recently filed a patent on oxidized Au on dispersed Ti catalysts, in which selectivities of only 97% were reported after 168 h on stream, suggesting by-product formation (34).

Based on our results, the formation of adsorbed by-products is due to the presence of acidic Ti sites. To prevent the ring opening of PO, poisons may be added to block these sites. Thiele and Roland (35) have shown that for liquid-phase epoxidation this approach can be successful. By addition of a neutral salt (such as Na₂SO₄) the sites with high acidity were neutralized, while the active Ti site remained active. Selective blocking of acidic sites will be the subject of future investigations.

5. CONCLUSIONS

Irreversible adsorption of propene oxide was observed on both a 1 wt% Au/TiO₂ and a 1 wt% Au/TiO₂/SiO₂ catalyst, yielding bidentate propoxy moieties. Spectroscopic evidence for oligomerization or dimerization of PO was not found. Similar propoxy species were observed after prolonged exposure of the catalysts to a propene/oxygen/hydrogen mixture. Additionally, formate and acetate species were formed exclusively on the Au/TiO₂ catalyst after exposure to the reacting mixture at 400 K or decomposition of the adsorbed bidentate propoxy species in a hydrogen/oxygen mixture. Supporting Au and TiO₂ on SiO₂ apparently reduces the activity toward C–C bond breaking. Based on the spectroscopic results, deactivation of Au/TiO₂ catalysts is likely related to the irreversible adsorption of a propoxy species on the active Ti site. On the TiO₂/SiO₂ catalyst the acidic Ti sites that cause ring opening of PO are apparently not located near the active epoxidation center. Therefore, no deactivation of the dispersed Ti catalysts was observed. Analysis of the Au/TiO₂/SiO₂ catalyst showed the formation of acetone and propanal. However, these side-products initially remain adsorbed on the catalyst surface under reaction conditions, maintaining a gas-phase selectivity of >99%.

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