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Acrylate and propoxy-groups: Contributors to deactivation of Au/TiO_2 in the epoxidation of propene

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ABSTRACT

Reaction pathways of propene in the selective propene epoxidation over Au/TiO_2 are discussed on the basis of *in-situ* IR spectra. A non-selective route for conversion of propene *via* acrylate to carboxylates and carbonates is demonstrated, likely contributing to catalyst deactivation. Propoxy-groups are predominantly formed by reaction of the catalyst surface with the reaction product propene oxide (PO), and are highly stable under reaction conditions. These propoxy-groups are considered as deactivating species, and not as intermediates for the production of PO, or carboxylates and carbonates.

1. Introduction

The gas-phase epoxidation of propene is a promising alternative process for the conventional propene oxide manufacturing methods that have economical and ecological disadvantages [1]. In 1998, Haruta et al. found that highly dispersed Au/TiO_2 catalysts were selective for the epoxidation of propene in the presence of both oxygen and hydrogen, yielding propene oxide with selectivity higher than 90% and conversions in the range of 1–2% [2]. Key factors determining the catalytic activity of gold-titania are the size of the gold particles, the applied method for Au deposition, and the origin of the support material [3]. Au/TiO_2 does not show stable performance. Only isolated Ti-sites, such as those created on TiO_2–SiO_2, TS-1, TS-2, Ti-zeolite β, Ti-MCM-41, Ti-MCM-48, or Ti-SBA-15 [4–10], provide for catalyst stability.

The mechanistic pathway of the epoxidation reaction over gold-titania catalysts has received considerable attention in the literature and very likely involves the formation of hydroperoxide-like species [1,11–15]. It has been reported that hydrogen and oxygen can react on small gold particles to form these hydroperoxide-like species, which further react with propene to produce propene oxide over isolated Ti-sites [4,5,11]. The role of gold in the activation of propene and the deactivation mechanism of Au/TiO_2 catalysts are still a matter of debate. Infrared spectroscopy was used to show that the interaction of propene with Au/TiO_2 catalysts was reversible and formation of bidentate propoxy species on the catalyst surface was observed only after exposure to the reaction mixture of propene, and both H_2 and O_2 in nitrogen [16]. It was proposed that these species were formed by ring opening of the product propene oxide. Deactivation of the catalyst could be the result of irreversible adsorption of these bidentate propoxy species [16]. Alternatively, it has also been proposed that propene is activated over Au, directly producing these bidentate propoxy species. These propoxy species are then considered as important intermediates in the oxidation pathway to yield propene oxide [1,17,18].

In this paper, we present additional Diffuse Reflectance Infrared Fourier Transformed (DRIFT) spectra of relevance to reveal the reaction mechanism of the epoxidation of propene over Au/TiO_2 catalysts. Compared to our previous study [16], we significantly prolonged the time of exposure of the catalyst system to propene, and further analyzed the reactivity of propoxy species adsorbed on the catalyst surface in H_2 and O_2 mixtures. Based on the spectroscopic observations, the chemistry of (Au-activated) propene on TiO_2 is discussed to include acrylate formation, a precursor of deactivating species such as carboxylates. Furthermore, the conclusion

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is drawn that bidentate propoxy species should also be considered contributors to deactivation of gold-titania catalysts, rather than important intermediates in the formation of Propene Oxide (PO).

2. Experimental

2.1. Catalysts preparation

Degussa P-25 titania was the standard support material used to prepare Au/TiO_2 catalysts, according to the literature [18]. Briefly, catalysts containing 1 wt% Au were prepared by deposition–precipitation of $Au(OH)_3$ at pH 9.5 and ambient temperature. The support (5 g) was dispersed in demineralized water (100 mL) and 2.5% ammonia was used to adjust the pH between 9 and 10. An aqueous solution of $HAuCl_4$ (77 mg/40 mL) was slowly added over a period of 15 min to the support, maintaining the pH at ~9.5 with 2.5% ammonia. The mixture was stirred for one more hour after which it was filtered and washed with demineralized water to remove chloride. The catalyst was dried overnight at 333 K and was calcined by heating from room temperature to 393 K (5 K/min) for 2 h and then to 673 K (5 K/min) for 4 h in static air. Characterization of the catalyst by TEM (Transmission Electron Microscopy) showed that Au particle sizes were in the range of 4–6 nm, as expected [16,18].

2.2. Drifts experiments

DRIFTS experiments were performed on a Thermo Nicolet Nexus IR, equipped with a SpectraTech DRIFT accessory. About 50 mg of the catalyst was treated in a flow of He (25 ml/min) at 323 K for 30 min before each experiment. Thereafter, the background spectrum of the sample was recorded (in He), using co-addition of 128 scans and a resolution of 4 cm^{-1}. Subsequently, the catalyst was exposed to various gas mixtures for prolonged periods of time. A feed of 10% propene in He, or, for reaction experiments, 10% propene, 10% H_2, and 10% O_2 in 70% He, was used. The adsorption of 1,2-propanediol was performed by saturation in a He flow at room temperature. The exposure to these reaction mixtures was followed by desorption experiments in He-flow. All experiments were performed at 323 K using a gas flow rate of 25 ml/min.

3. Results

3.1. Propene adsorption

The spectra obtained after propene adsorption (adsorption time of 20 min) and subsequent desorption in He at 323 K are shown in Fig. 1. The interaction of propene with the catalyst is not completely reversible. After 5 min of He flow, the remaining spectrum shows bands at 1682, 1636, 1550, 1437, and 1372 cm^{-1}. These absorptions in the 1700–1300 cm^{-1} region can be attributed to acrylate, in agreement with the literature data [19]. The C=O stretching vibration appears at 1682 cm^{-1} and the band located at 1636 cm^{-1} can be assigned to the C=C double bond stretching vibration. The broad signal at 1550 cm^{-1} can be assigned to asymmetric and symmetric O–C–O stretching vibrations of acrylate, and the 1437 cm^{-1} and 1372 cm^{-1} bands to CH bending modes. Additional evidence for the formation of acrylate is provided by the spectral region from 3200 to 2700 cm^{-1} (Fig. 1, inset). The bands at 2935 cm^{-1} and 2865 cm^{-1} are in excellent agreement with the C–H stretching modes of adsorbed acrolein and acrylate, as reported in [19]. A vibration at around 3080 cm^{-1}, indicative of $=CH_2$ is not observed, again in agreement with the reference spectra shown in [19]. Apparently this vibrational mode of acroleine and acrylate gives rise to very weak IR intensities when adsorbed on TiO_2 surfaces. Over time, the intensity of characteristic absorptions of acrylate decrease with remaining bands at 1617, 1576, 1471, 1438, and 1371 cm^{-1} (Fig. 1a). These remaining bands can be attributed to a mixture of formate and carbonate species [20,21]. The bands located at 1576 and 1438 cm^{-1} and 1371 cm^{-1} can be assigned to symmetric and asymmetric O–C–O stretch vibrations and the C–H bending modes of formate and acetate species, respectively. Finally, the bands at 1617 and 1471 cm^{-1} can be attributed to $\upsilon_{as}(CO^{2-})$ and $\upsilon_s(CO^{2-})$ of monodentate car-

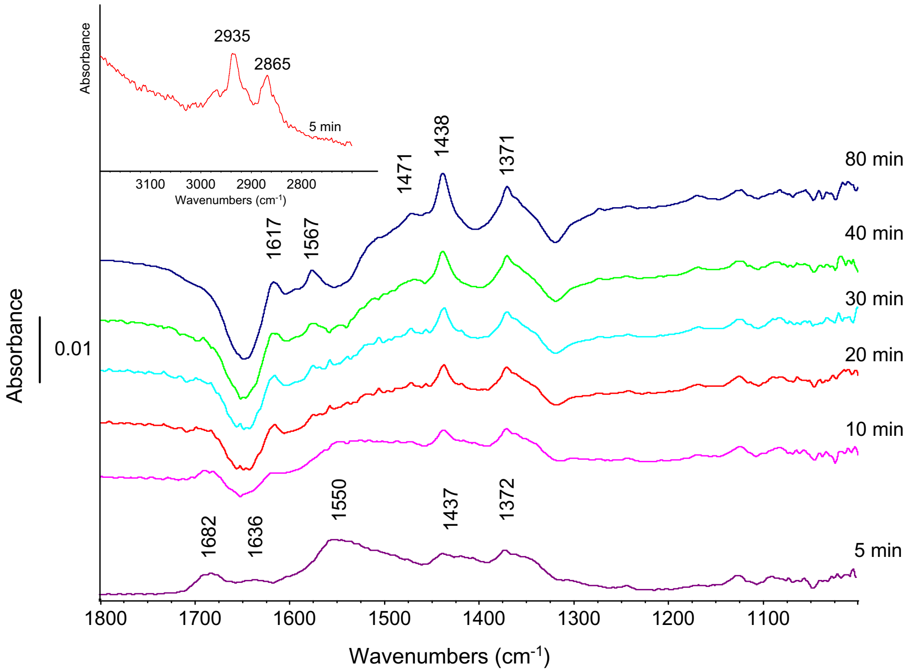

Fig. 1. DRIFT spectra of Au/TiO_2 catalyst recorded in He at 323 K (5–80 min) after a period of 20 min of propene adsorption. The inset shows the spectral region of 2700–3200 cm^{-1} of the spectrum recorded after 5 min in He.

bonate. It should be noted that the interaction of propene with the titania P25 support was completely reversible, suggesting that gold, in combination with the TiO_2 support, promotes partial oxidation of propene to acrylate and products of consecutive oxidation in small quantities. As a final note, bands in the region around 1100 cm^{-1} have been observed in [17] upon interacting propene with the catalytic material, while in our experimental conditions these bands are barely visible.

3.2. Adsorption of 1,2-propanediol

Species obtained from the adsorption of 1,2-propanediol are quite different from those obtained for propene adsorption/desorption (cf. Figs. 1 and 2). After He-flush, bands at 1456, 1375, 1336, 1227, 1142, and 1096 cm^{-1} appear as shown in Fig. 2. In the CH stretching region (not shown) absorptions of $\upsilon_{as}(CH_3)$ at 2964 cm^{-1}, υ_{as} (CH_2) at 2927 cm^{-1}, and $\upsilon_s(CH_2)$ at 2869 cm^{-1} were observed. The bands at 1456, 1375, and 1336 cm^{-1} can be assigned to $\delta_{as}(CH_3)$, $\delta_s(CH_3)$, and $\delta_s(CH)$, respectively. In this case also C–O–Ti stretching vibrations at 1142 and 1096 cm^{-1} can be observed in the spectrum, indicating that the interaction of 1,2-propanediol with the Au/TiO_2 catalysts produces bidentate propoxy species, in agreement with previous studies [16,18].

Subsequently, a mixture of H_2 and O_2 was added to the propoxylated catalyst surface, to elucidate the role of bidentate propoxy species in the gas-phase epoxidation reaction. The spectra are also shown in Fig. 2. The presence of H_2 and O_2 did not produce significant changes in the features of the spectra. The signals corresponding to bidentate propoxy compounds are of constant intensity, and the characteristic absorptions of propylene oxide or rapid decomposition to carboxylates/carbonates were not observed under the applied reaction conditions.

3.3. In-situ reaction

A fresh batch of catalyst was exposed to consecutive cycles of the reaction mixture of 10% propene, 10% H_2, and 10% O_2 in 70% He for 10 min, followed by 30 min of He-flush. The obtained spectra are shown in Fig. 3. The interaction of the catalyst with the reaction mixture yields spectral features very similar to those presented in Fig. 2, with bidentate propoxy species dominating. Adsorption of these species was completely irreversible since the intensity of the characteristic bands was constant in the period of the 30-min He-flush (not shown). In addition, the spectra show features at 1684 and 1537 cm^{-1} consistent with the formation of acrylates (compare Fig. 1).

Consecutive reaction causes an increased intensity of the bidentate propoxy species. This is in agreement with irreversible adsorption of this compound on Au/TiO_2 in reaction conditions. It should be noted that mass spectrometer analysis obtained during exposure of the catalyst to the consecutive reaction cycles indicated a decrease in propene oxide (m/e 58) production, suggesting that deactivation of the catalyst occurs.

4. Discussion

4.1. Activation of propene

In the present study, propene adsorption over the applied Au/TiO_2 catalyst was found to be irreversible, and was shown to lead to the formation of acrylate by partial oxidation over Au/TiO_2. This is a novel finding, and was not observed in previous studies [16–18]. This is very likely the result of the different times to which the catalyst was exposed to propene, which was ~5 min in [16], *versus* 20 min in the present study. Furthermore, the time passed after introduction of He to the feed-lines and IR cell to remove adsorbed propene will also determine what is spectroscopically observed. This is illustrated by the consecutive spectra in He (Fig. 1), which show a transformation of acrylates to formate and carbonate species. The spectrum starts to show very similar features as reported by Nijhuis in their careful IR study reported in [17,18], who also assigned the spectral features to carboxylate/carbonate species. Fig. 4 shows a schematic representation of the transformations that we believe are representative for the surface chemistry of propene over Au/TiO_2. The acrylate route is one of the options, leading to catalyst deactivation. Gold particles catalyze this oxidation reaction, since

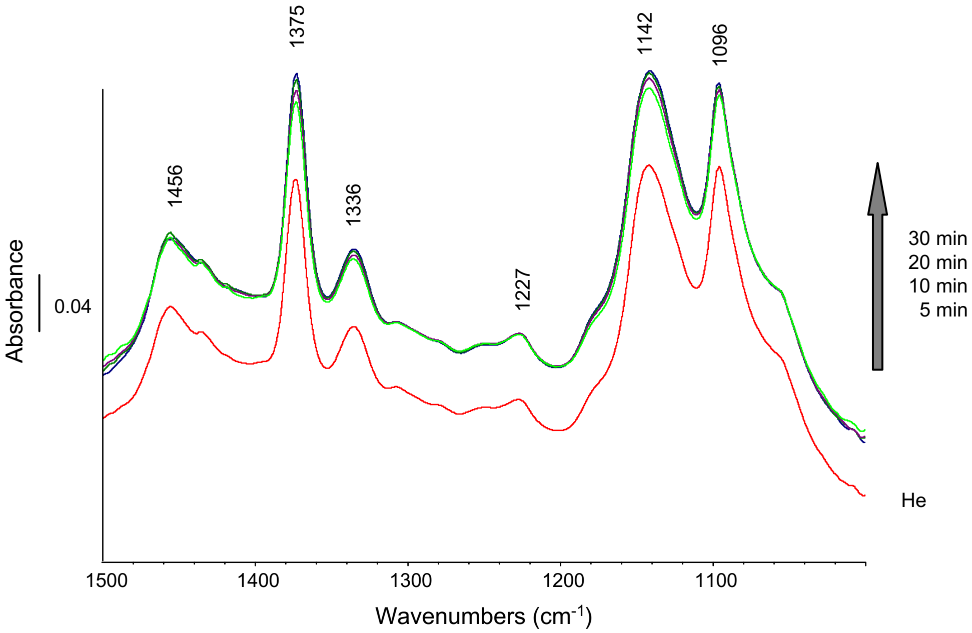

Fig. 2. DRIFT spectra of the Au/TiO_2 catalyst after 45 min of 1,2-propanediol adsorption, and purging for 60 min in He (bottom spectrum). The top five spectra were recorded in a $H_2 + O_2$ mixture (H_2:O_2:He = 10:10:80) at 323 K after various time intervals.

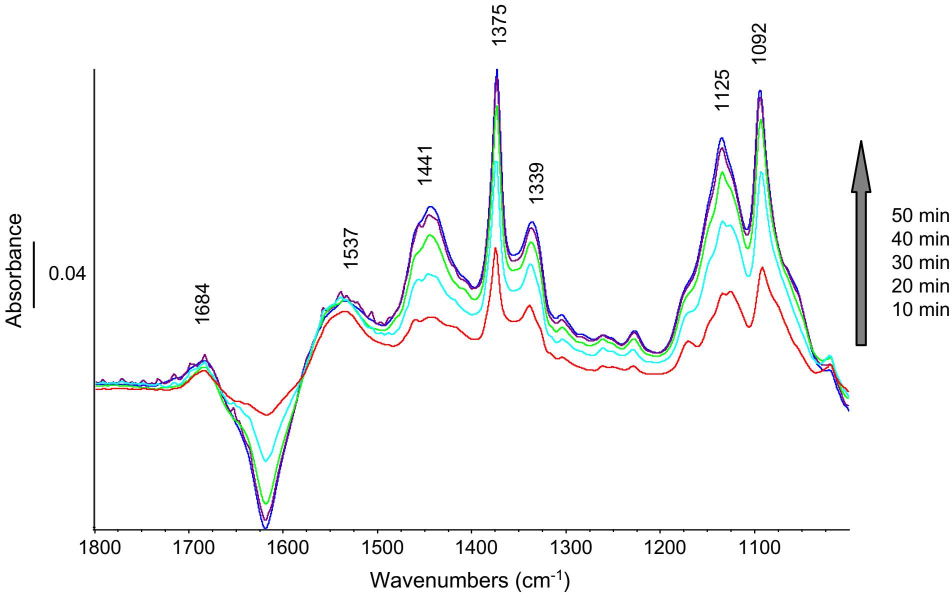

Fig. 3. DRIFT spectra of Au/TiO_2 catalyst recorded in He at 323 K, purged for 30 min after 10-min intervals of treatment in the reaction mixture (H_2:O_2:C=C–C:He = 10:10:10:70). The total reaction time is indicated in the figure.

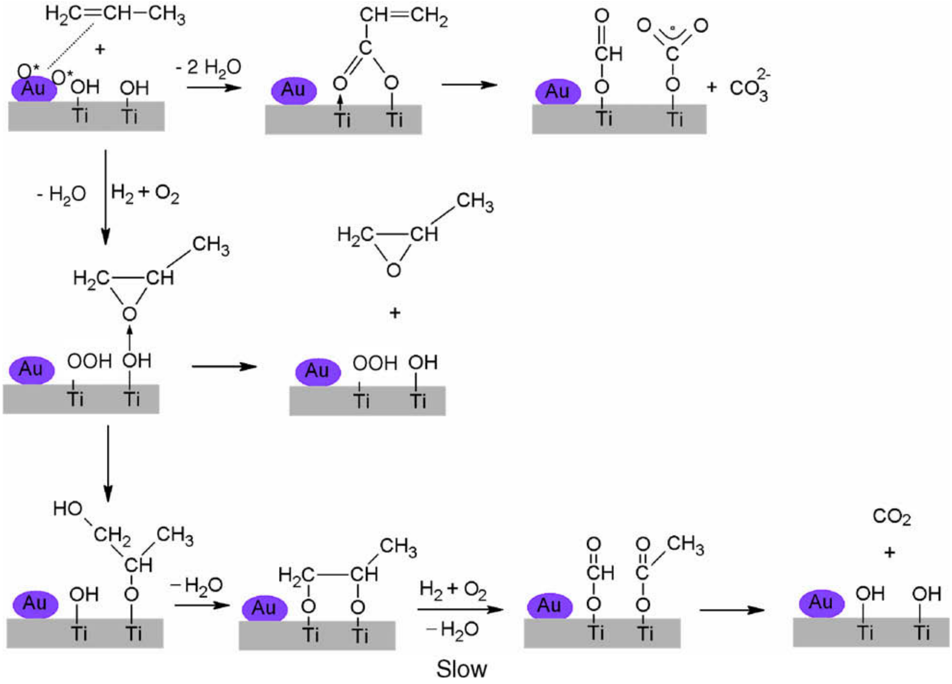

Fig. 4. Proposed reaction steps in the epoxidation of propene over Au/TiO_2 catalysts.

formation of surface-adsorbed oxygenates was not detected over a bare titania support. The source of oxygen for this reaction could be oxygen adsorbed on the surface of Au, which is in agreement with a study of Friend et al. on the partial oxidation of propene over oxygen-covered Au(1 1 1) [22]. The work of these authors shows that propene oxidation occurs on Au(1 1 1) covered with an oxygen layer. Insertion of oxygen into the allylic C–H bond of propene yields an allyloxy intermediate, which ultimately produces acrolein [22]. The oxidation of acrolein yields combustion products (CO_2 and H_2O). The formation of deactivating carbonate/carboxylate surface species *via* an acrylate intermediate can thus be expected. The role of Au in the activation of propene is also in good agreement with a recent study of Nijhuis et al., who nicely demonstrated this by XANES measurements and determination of an inhibiting effect of propene on the reaction of hydrogen and oxygen over the catalyst [23]. The findings reported here are somewhat different from that reported in Ref. [17] in which activated propene is proposed to be transferred to the TiO_x patches nearby the Au leading to formation of bidentate propoxy species. The propoxy species are suggested to be reactive intermediates in [17], leading to (i) the formation of PO and (ii) deactivation products, such as carboxylates. The importance of propoxy species in the reaction mechanism will be further discussed in the following.

4.2. Role of bidentate propoxy species in the reaction pathway

The present study confirms several aspects of the chemistry of C_3-alcohols and PO on the surface of Au/TiO_2 reported previously [16–18]. The interaction of propene oxide with Au/TiO_2 catalyst is irreversible, while decomposition of propene oxide, produced in the reaction, by ring-opening yields bidentate propoxy species. This observation is also in agreement with the work of Sun et al., who indicated that propene oxide could easily open its ring under acid catalysis condition or alkali catalysis condition, because of the large ring strain of propene oxide. Ti-sites are Lewis acids and the ring-opening reaction of propene oxide easily occurs under the applied reaction conditions [24].

Bidentate propoxy species have been considered to be a reaction intermediate in the gas-phase epoxidation of propene [1,18], formed by direct interaction of propene with the catalyst. Peroxide species formed by reaction of H_2 and O_2 over Au were proposed to aid in the desorption of the bidentate propoxy species from the catalyst, producing propene oxide. The spectra obtained in the present study did not show changes in position or intensity of characteristic bands of bidentate propoxy species in the presence of H_2 and O_2. Furthermore, features of propene oxide could not be detected within 30 min (Fig. 2). These results indicate that propene oxide formation from bidentate propoxy species is unlikely. As indicated in Fig. 4, we prefer the route of direct oxidation of propene to PO by surface hydrogen peroxide species on Ti-sites [13,14]. The first step in the selective reaction pathway is the formation of hydrogen peroxide from H_2 and O_2 reaction over gold nanoparticles. This produces Ti-hydroperoxide species on Ti centers (Fig. 4). Ti-hydroperoxide species will react with propene to form propene oxide. The same mechanism is proposed for the epoxidation of propene in the liquid phase over isolated Ti-sites in the presence of H_2O_2.

Recently, *in-situ* UV–Vis diffuse reflectance spectroscopy was used in combination with Ti K-edge XANES by Oyama et al. to study the formation of Ti-hydroperoxo species over Au-Ba/Ti–SiO_2 catalyst. It was shown that Ti-hydroperoxide species formed during propene epoxidation might be the true reaction intermediate [15]. Oyama et al. also concluded that propylene oxide production via reaction of bidentate species is unlikely. They suggested that this species was probably a spectator [15]. In the present study, the spectral observations after exposure of the catalyst to several reaction cycles (Fig. 3) showed an increase in the amount of adsorbed bidentate propoxy species on the surface of the catalyst. At the same time, analysis of the gas-phase showed a reduction in propene oxide production. Irreversible adsorption of bidentate propoxy species is therefore very likely responsible for deactivation of the Au/TiO_2 catalyst [16]. The experiment shown in Fig. 3, however, suggests that the contribution of the decomposition of the propoxy-groups to the formation of carboxylates and carbonates might be relatively small [16]. The direct non-selective activation of propene *via* acrylate to these species might be more significant (Fig. 4).

5. Conclusions

Propene adsorbed on Au/TiO_2 can be transformed to an acrylic intermediate, a precursor of formate and carbonate species. This step should be considered as another reaction step toward catalyst deactivation. Propoxy-groups were not produced by irreversible propene adsorption, but only by the ring-opening reaction of the product PO. These propoxy-groups mainly contribute to catalyst deactivation and are likely not an important intermediate in the conversion of propene to PO over Au/TiO_2 catalysts.

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