Heterogeneous Catalysis

The Role of Gold in Gold–Titania Epoxidation Catalysts**

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Catalysts consisting of gold nanoparticles on titania supports have received considerable attention over the past years as novel systems for the direct and selective epoxidation of propene.[1–3] A process to directly epoxidize propene is highly desirable as the currently available processes are not optimal. The chlorohydrin process is being phased out because of environmental concerns, and each of the hydroperoxide processes [styrene monomer/propylene oxide (SM/PO) and propylene oxide/*tert*-butanol, (PO/TBA)] produces a by-product (styrene and *tert*-butanol, respectively) in a fixed amount, thus making the production capacity less flexible.

Gold–titania catalysts are able to epoxidize propene in the presence of a mixture of hydrogen and oxygen under very mild conditions (323–373 K and atmospheric pressure). Although these catalyst systems are highly selective, two main problems need to be addressed. The conversion remains quite low (typically below 2%, although conversions of up to 10% have been reported with certain promoters[4]) and the hydrogen efficiency is insufficient, typically 30%.[5]

Understanding the mode of operation of the catalyst would be a great help in improving the catalyst performance. The general assumption is that a reaction takes place, in which a peroxide species is formed from hydrogen and oxygen on gold particles, and the propene would then be epoxidized over Ti sites.[3,6] It is known that titania acts as an epoxidation catalyst in the liquid phase when hydrogen peroxide is the oxidant.[7] It has also been shown that gold catalysts are capable of producing hydrogen peroxide from hydrogen and oxygen.[8] However, attempts to prove that this reaction occurs during the gas-phase epoxidation of propene with hydrogen and oxygen have so far been unsuccessful. Our ongoing Raman spectroscopy study of the catalyst has not yet shown the presence of any peroxide species during the reaction, even though the sensitivity of Raman spectroscopy towards peroxides is high.[9]

The low yield of product obtained from gold–titania catalysts is usually explained by a strong adsorption of propene oxide on the catalyst.[4,5] In this work the adsorption behavior of propene, propene oxide, and related species on titania and gold–titania is investigated by use of IR spectroscopy to get a better understanding of the events on the catalyst surface, and to thus allow the development of a reaction mechanism and a better catalyst.

Prior to the spectroscopic study, the catalyst activity was verified:[9] the epoxidation activity of the catalyst comprising 1 wt% Au on P25 titania was 0.9% conversion, 99% selectivity at 323 K, and a gas hourly space velocity (GHSV) of 6000 h^{-1} (mixture of 10% O_2, H_2, and propene in He). This catalyst performance is comparable to the reported activity for similar catalysts.[1,3,10]

When the adsorption and subsequent desorption of propene on the bare titania P25 support was measured, no bands remained, thus indicating a completely reversible physical adsorption. This is in full agreement with the observation of Mul and co-workers.[11] However, when the same experiment was performed with the Au/TiO_2 catalyst, the adsorption was no longer reversible. In Figure 1 the IR spectra of both samples after desorption of physisorbed propene are shown. Evidence of residual species on the surface of the Au/TiO_2 catalyst is clearly visible in the corresponding spectrum, whereas for titania only a small decrease in the absorption at 1650 cm^{-1} is observed owing to a slight decrease in water content, which also causes a negative

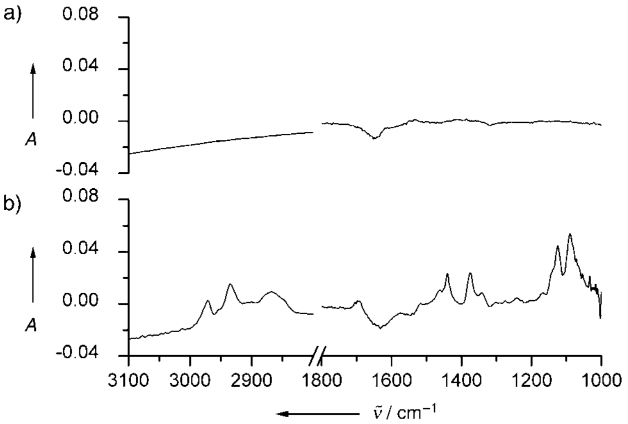

Figure 1. IR spectra of adsorbed species on the a) titania support and on the b) gold-on-titania catalyst after adsorption and subsequent desorption of propene (323 K; 100 spectra averaged).

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background at higher wavenumbers. In the IR spectrum of the gold-on-titania catalyst, bands appear at 2970, 2935, 2870, 1460, 1440, 1375, 1340, 1130, and 1090 cm^{-1}. As the catalyst was exposed only to propene, it is apparent that gold plays a more elaborate role in this catalyst system than was generally assumed, namely, that the gold is just providing peroxide for the epoxidation with propene on titania. The bare titania on which the propene was absorbed was titania from a blank catalyst preparation (i.e., prepared in the same way as the gold catalyst but without the addition of $AuCl_3$). Therefore the different adsorption behavior of propene can only originate from the gold and not from changes to the titania during the preparation of the catalyst.

The bands in the 1050–1150-cm^{-1} region are characteristic of C–O–Ti stretching vibrations,[11,12] thus indicating that an adsorbed species remains on the titania support. To make the identification of this residual species more facile, experiments were performed in which different components were adsorbed and desorbed on the P25 support. Propene oxide, 1,2-propanediol, 1-propanol, and 2-propanol all adsorbed irreversibly on (i.e., reacted with) titania. The spectra of species remaining after adsorption/desorption are given in Figure 2a. In the CH stretching region, the main bands that can be observed are usually assigned as $\nu_{as}(CH_3)$ at 2970, $\nu_{as}(CH_2)$ 2935, $\nu_s(CH_3)$ 2900, and $\nu_s(CH_2)$ at 2870 cm^{-1}. In the CH bending region $\delta_{as}(CH_3)/\delta(CH_2)$ at 1460, $\delta_s(CH_3)$ at 1375, and $\delta(CH)$ at 1335 cm^{-1} can be assigned. The bands at 1090 and 1140 cm^{-1} can be assigned as the C–O–Ti stretching vibrations for primary and secondary carbon atoms, respectively. The structures of the most likely species as they are formed on the titania surface are given in Figure 2b.

When the difference spectrum for propene adsorbed/desorbed on the gold-on-titania catalyst in Figure 1 is compared to the spectra in Figure 2, it is clearly quite similar to that of the species on the surface of titania after adsorption of propene oxide or propanediol. The source of the oxygen atom in this component is unclear, but it probably originates from titania O or OH groups. The formation of this species can only be explained by considering a key role played by gold: propene adsorbs onto gold, and this adsorbed and activated species then reacts with surface O(H) groups of the titania. Alternatively, the gold might influence the reactivity of the nearby titania, thus making it react more easily with propene. The fact that the intensities of the peaks of the spectrum in Figure 1b are relatively low (absorbance is about 20 times lower than that in Figure 2), can be easily explained by the relatively low gold loading of 1 wt %, which makes only a small portion of the titania surface available for a reaction with propene. This can be observed in the TEM micrograph in Figure 3 in which the gold particles occupy only a small part of the titania.

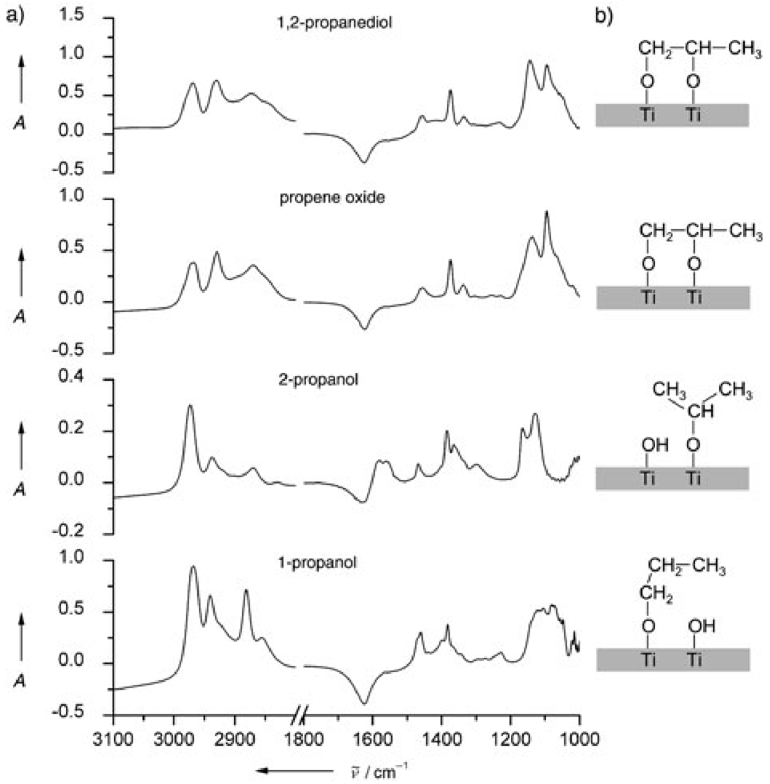

Figure 2. a) IR spectra after adsorption and subsequent desorption of 1,2-propanediol, propene oxide, 2-propanol, and 1-propanol on titania (323 K). b) Most likely structures of the adsorbate species that correspond to the IR spectra in a) (20 spectra averaged).

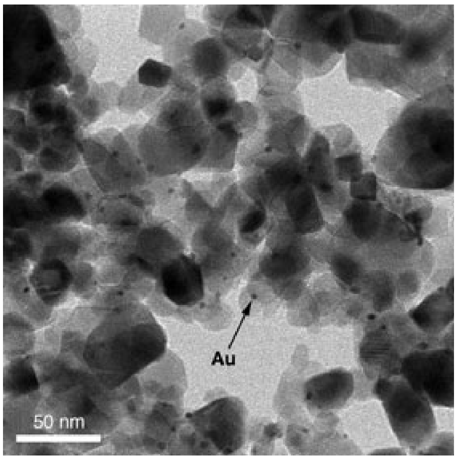

Figure 3. TEM micrograph of 1 wt% gold on titania (P25) catalyst.

The only real difference between the spectrum in Figure 1b and the spectra in Figure 2 for adsorbed propene oxide and 1,2-propanediol is the intensities of the bands at 1440 and 1370 cm^{-1}. Over time, the intensity of these bands increases further, even when the catalyst is kept in a helium gas stream, whereas the intensity of the other bands decrease very slowly (Figure 4). In addition, a broad band appears at 1500–1550 cm^{-1}. The bands that grow in intensity can be attributed to carbonate/carboxylate species.[13,14] The fact that the intensities of the CH stretching bands do not increase supports this assignment. The formation of carbonates/carboxylates can be explained by the slow oxidation of bidentate propoxy species. This oxidation reaction must be catalyzed by the gold particles, as it is not observed when the bidentate propoxy species is formed on bare titania by the adsorp-

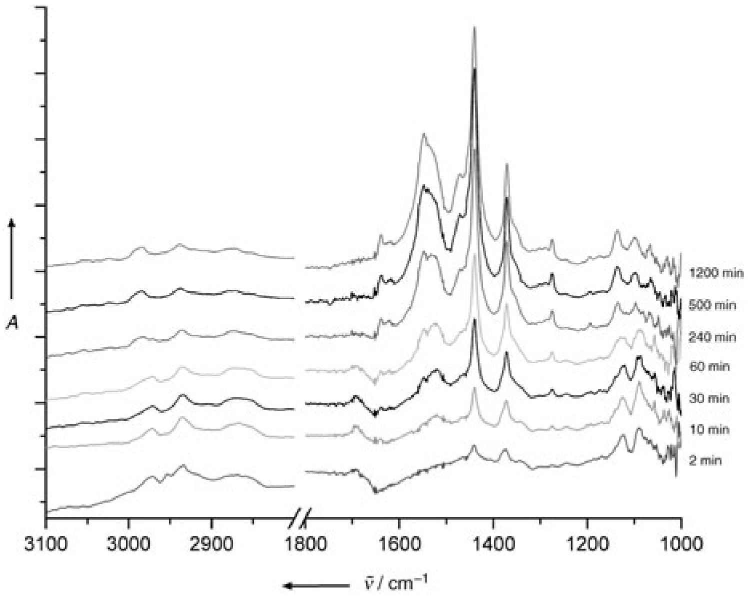

Figure 4. Spectra that demonstrate the gradual oxidation of a bidentate propoxy species on the gold–titania catalyst. Spectra were recorded from 2 to 1200 min after exposure of the catalyst to propene for 2 min (323 K; 10 spectra averaged).

tion of propene oxide or 1,2-propanediol. Furthermore, formation of carbonates/carboxylates may partly explain why gold–titania catalysts slowly lose activity during epoxidation. The fact that a calcination procedure removes these species from the surface[13] concurs with the observation that the catalyst largely regains its activity for epoxidation after calcination. Additional evidence that these carbonate/carboxylate species are key to the deactivation of the catalyst comes from the fact that they could not be observed on a catalyst consisting of gold on a dispersed titania support.[9] This type of catalyst is known to be much more stable towards deactivation.[3,15]

An additional experiment was performed in which a mixture of gas comprising 10 % propene, 10 % oxygen, 10 % hydrogen, and the rest helium was fed to the Au/TiO_2 sample for only 3 min. Figure 5 shows the IR spectrum of the adsorbed species 3 min after removal of the propene feed. The presence of hydrogen and oxygen results in much more intense bands of the bidentate propoxy species in a shorter time. In the presence of hydrogen/oxygen it is observed that the bidentate propoxy species is slowly oxidized on the catalyst surface (similar to the situation evinced in Figure 4). However, the rate at which the bidentate propoxy bands decrease in intensity is slightly higher, thus indicating that desorption occurs. The species formed by the oxidation of the bidentate propoxy species in the presence of hydrogen and oxygen are a little different as bands at 1350 and 1720 cm^{-1} also appear. Increasing the temperature to 373 K results in the complete disappearance of the bands of the bidentate propoxy species (only the carbonate/carboxylate bands remain), which was not the case when a similar experiment was performed in a helium stream. It is likely then that hydrogen and oxygen aid the desorption of this species. Further work is needed to verify whether the desorbing species is indeed propene oxide. However, this assumption seems likely to be the case, as propene oxide is the only product in catalytic experiments carried out under mild conditions.

In summary, the role of gold in the epoxidation of propene is more than that generally assumed, namely, that gold merely provides a peroxide species, which subsequently epoxidizes propene on the titania sites. An IR spectroscopic study has shown that the presence of gold nanoparticles on titania catalyzes a reaction between propene and the titania sites. A bidentate propoxy species is produced, similar to that formed when propene oxide is absorbed on titania. The gold particles also catalyze a consecutive oxidation of the bidentate propoxy species to form carbonate/carboxylate species, which is possibly the cause of catalyst deactivation. In the presence of hydrogen and oxygen the bidentate propoxy species can desorb from the catalyst surface. Therefore it is likely this species is a reaction intermediate in the epoxidation of propene.

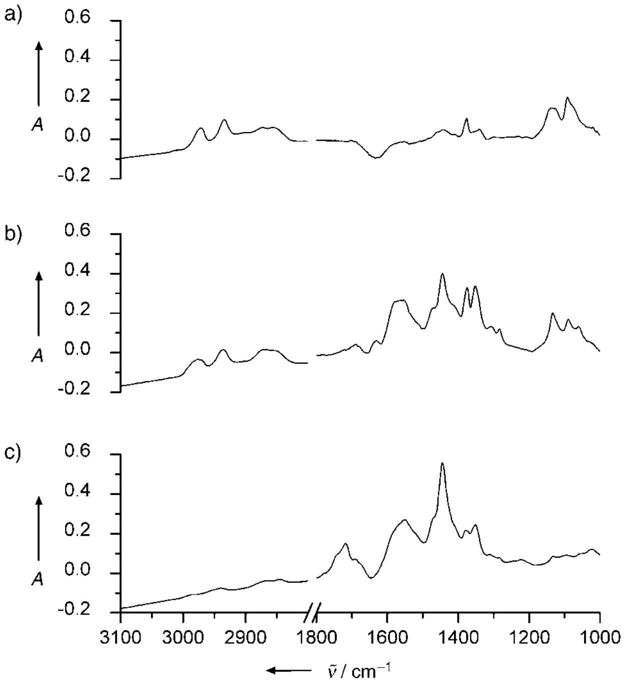

Figure 5. Spectra recorded after 3 min passage of a gas stream comprising 10 % H_2, 10 % O_2, and He (323 K). a) 3 min after removal of propene; b) after 3 h; c) 30 min after the temperature was increased to 373 K (50 spectra averaged).

Experimental Section

Highly dispersed gold-on-titania catalysts were prepared by a deposition/precipitation method. A solution of $AuCl_3$ in water was slowly added to a stirred suspension of P25 titania in water. The pH of the water was kept at 9.5 with aqueous ammonia. After the catalyst had been aged for 30 min, it was filtered and washed three times with deionized water. The catalyst was dried in air overnight at 393 K and calcined for 4 h at 673 K (10 K min^{-1} heating and cooling rate). TEM analysis showed a narrow size distribution for the gold particles (3.2–4.2 nm), although there were a few smaller and larger particles, all of which were in the range of 2–6 nm. X-ray fluorescence (XRF) analysis showed the amount of chlorine on the catalyst (a known promoter) to be lower than the detection limit of 7 ppm. The only contaminant present in a significant quantity was nickel (200 ppm), which was also present in the P25 used. Catalytic testing showed a propene oxide yield of up to 0.5 % at 323 K and a space velocity of 6000 h^{-1} with a gas mixture of 10 % propene, 10 % hydrogen, and 10 % oxygen in helium.

Adsorption experiments were performed with a Perkin Elmer Spectrum One IR transmission spectrometer with self-supporting catalyst wafers of 100–120 micrometer thickness (pressed at 1.5 ton from powdered catalyst). Prior to the adsorption–desorption experiment the samples were dried in situ by heating them to 573 K in helium, and then the samples were cooled to 323 K. For liquids, adsorption measurements were performed by pumping either 400 $\mu l h^{-1}$ of liquid in a He stream of 25 $mL min^{-1}$ (at 353 K) fed through an IR cell for 10 min, after which only helium was fed, and the desorption was measured. Propene adsorption was measured similarly with a gas stream of 5 $mL min^{-1}$ of propene in 25 $mL min^{-1}$ of helium. During the desorption in helium, spectra were measured until no changes were observed. The spectra of the samples at 323 K prior to the adsorption were used as background.

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