

In Situ UV–vis and EPR Study on the Formation of Hydroperoxide Species during Direct Gas Phase Propylene Epoxidation over Au/Ti–SiO₂ Catalyst

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Received: September 14, 2006; In Final Form: October 16, 2006

In recent years, there have been great experimental and theoretical advances in the understanding of the epoxidation of propylene by O₂ and H₂ over Au supported on titanium-containing oxidic supports; however, thus far spectroscopic evidence of reacting species for proposed mechanisms has been lacking. Hydroperoxide species have been postulated as an intermediate responsible for the epoxidation of propylene with O₂ and H₂. In order to obtain direct evidence for the different type of active oxygen species, in situ UV–vis and EPR measurements were carried out during the epoxidation of propylene with O₂ and H₂ over a Au/Ti–SiO₂ (Ti/Si = 3:100) catalyst. It was determined that the adsorbed species of oxygen (O₂[–]) resided on Au, more likely at a perimeter site, and it led to the formation of titanium hydroperoxo species. These results support the possible mechanism of formation of these hydroperoxo species via H₂O₂ produced from O₂ and H₂ adsorbed on the Au surfaces.

Although bulk gold was regarded for a long time as a poorly active catalyst, gold nanoparticles deposited on a variety of metal oxides are surprisingly active for many reactions, including direct vapor-phase oxidation of propylene to propylene oxide (PO).¹ Propylene oxide is an important bulk chemical with a world production of about 6 million tons per year. It is used for manufacturing a wide variety of derivatives, among which polyether polyols and propylene glycol are the main end products.² The viability of the vapor-phase epoxidation of propylene over Au nanoparticles supported on Ti-based oxides such as TiO₂,^{3,4} TiO₂–SiO₂,⁵ TS-1,⁶ Ti–MCM-41,⁷ Ti–MCM-48,⁸ Ti-containing hydrophobic silsesquioxanes⁹ and three-dimensional (3-D) mesoporous titanosilicates^{10–12} has been demonstrated throughout this decade. Recently, we have shown the possibility of PO production nearly at a commercial level of productivity over an Au/Ti–SiO₂ catalyst (Ti/Si = 3:100) with a steady space–time yield of PO of 1.1–1.4 × 10^{–3} mol h^{–1} gcat^{–1} at atmospheric pressure with a propylene conversion of up to 8.5%, a PO selectivity of 91%, and a hydrogen efficiency of 35%,¹² while Delgass's group has recently reported that a comparable or a little better performance could be obtained by Au deposited on TS-1 pretreated beforehand in NH₄NO₃ solution.⁶

In analogy to the well-studied liquid-phase epoxidation with hydrogen peroxide over TS-1, the formation of PO in gas phase on Au/Ti–SiO₂ catalysts may as well involve the formation of hydroperoxo species. For many years, the formation, charac-

terization, and reactivity of the hydroperoxo intermediates have been studied in depth by a plethora of experimental techniques.^{13–17} Recently, spectroscopic studies have proved the formation of Ti-peroxo/hydroperoxide species over Pd supported on different types of Ti containing zeolites¹⁸ and also on Ti-SBA-15 materials¹⁹ in methanol solution of H₂O₂. It has also been reported that organic hydroperoxides in liquid phase form a peroxo complex analogous to the hydroperoxo species formed by hydrogen peroxide.²⁰ To the best of our knowledge, except for the work by Goodman and his co-workers²¹ on inelastic neutron scattering for Au/TiO₂, there have not been published reports showing the presence of superoxo/hydroperoxo species detected by in situ experiments during propylene epoxidation with O₂ and H₂ in the gas phase over supported nanogold catalysts.

In this communication, we have conducted in situ UV–vis and EPR characterization measurements to investigate the formation of the hydroperoxo species on the surfaces of Au/Ti–SiO₂ (Ti/Si = 3:100) catalyst under similar conditions to those of the gas-phase propylene epoxidation reaction.^{10–12} The EPR study was carried out in a specially designed cell consisting of a fixed-bed reactor connected with the EPR tube so that EPR-active species can be trapped and detected at any desired stage (see Supporting Information).

The mesoporous titanosilicate was prepared following the method described by Sinha et al., adjusting the amount of the titanium source in order to have a Ti/Si molar ratio of 3.¹⁰ The Au/Ti–SiO₂ catalyst was prepared by the deposition–recipitation (DP) method. In a typical synthesis, a solution of HAuCl₄·4H₂O (0.062 g) in water (150 mL) was heated to 343 K, and the pH value was adjusted to 7.0 by addition of aqueous NaOH solution. The support powder (0.75 g) was dispersed and stirred in the solution, and the pH value was readjusted to 7.0. The

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suspension was stirred at the same temperature for 1 h. The solid was collected by filtration, dried under vacuum at room temperature for 12 h, and calcined in air at 573 K for 4 h. Titanium silicalite-1 (TS-1 Ti/Si = 1:100) was synthesized following the method by Khomane et al.²² Supported Au/Ts-1 catalyst was prepared in a fashion similar to that described for the mesoporous Au/Ti-SiO₂ material.

Typical reaction conditions for propylene epoxidation with Au/Ti-SiO₂ catalyst were as follows. Catalyst bed was pretreated at 523 K in a flow of 10 vol % H₂ in Ar for 30 min and then in a flow of 10 vol % O₂ in Ar for 30 min. Catalytic epoxidation was carried out by using 0.50 g of catalyst at 423 K with a feed containing 10 vol % of each C₃H₆, O₂, and H₂ in Ar (space velocity 4000 cm³ h⁻¹ gcat⁻¹). The catalytic performance of the Au/Ti-SiO₂ catalyst (Au nominal loading 4 wt %) was 2.3% in propylene conversion, 95% in PO selectivity, and 16% in H₂ efficiency (space time yield = 3.7×10^{-4} mol h⁻¹ gcat⁻¹).

In situ UV-vis diffuse reflectance spectra were recorded with a Cary 5000 Varian spectrometer equipped with a Harrick Scientific reaction chamber (model HVC-DRP) in conjunction with the praying mantis diffuse reflectance attachment (DRP-XXX). EPR measurements were carried out in a special glass reactor connected to the EPR sample tube (see Supporting Information). The catalyst sample was packed in the reactor, evacuated at 298 K and purged with Ar. Then samples were pretreated at the same conditions of the propylene epoxidation reaction. After reaction, the reactor was evacuated to remove all the gases present as dead volume. The EPR measurements were carried out in a JEOL EPR spectrometer (model JES-TE300) at liquid nitrogen temperature. The XANES spectrum was measured at BL12C in the Photon Factory, Institute for Material Structure Science, High Energy Accelerator Research Organization. Data were collected in transmission mode using I₀ and I ionization chambers filled with pure N₂ and 15 vol % Ar in N₂, respectively. A Si(111) double crystal was used as a monochromator. A glass XAFS cell with polyimide film windows was filled with a sample of the freshly calcined catalyst, and XAFS measurements were carried out at room temperature without any further treatment.

During the in situ UV-vis measurements we found not only the typical charge-transfer bands due to tetrahedral Ti⁴⁺ species near 43 000–45 000 cm⁻¹ (233–222 nm) and gold plasmon resonance band at 18 000–20 000 cm⁻¹ (556–500 nm) but also a broad feature in the 28 000 cm⁻¹ (360 nm) region as shown in Figure 1 (bottom). In order to obtain a better insight into the buried species apart from Ti⁴⁺ tetrahedral species the UV-vis spectra were referenced to pure titanosilicate support material instead of BaSO₄ as presented in Figure 1 (top). By analyzing the spectral data in this way, we avoid any peaks originated from the support itself before reaction. As reported in the literature, the interaction of H₂O₂ with the Ti⁴⁺ centers of Ti-zeolites generates a UV-vis broad band at around 27 000 cm⁻¹ (370 nm), which has been assigned to a charge transfer interaction between the hydroperoxide (–OOH) ligand and Ti⁴⁺.^{18,23,24} It is clearly observed from Figure 1 that this band intensity increases with the progress of the reaction.

Additional experiments were also carried out by soaking the titanosilicate material with liquid H₂O₂. The color of the sample changes to yellow and a broad feature emerges in the 26 000–33 000 cm⁻¹ (385–303 nm) region reproducing literature reports (see Supporting Information).²⁵ To explain the bands in this region, three main types of structures for TS-1,^{26,27} Ti-ZSM-12,²⁸ or zeolite-hosted mononuclear titanium oxide species²⁹

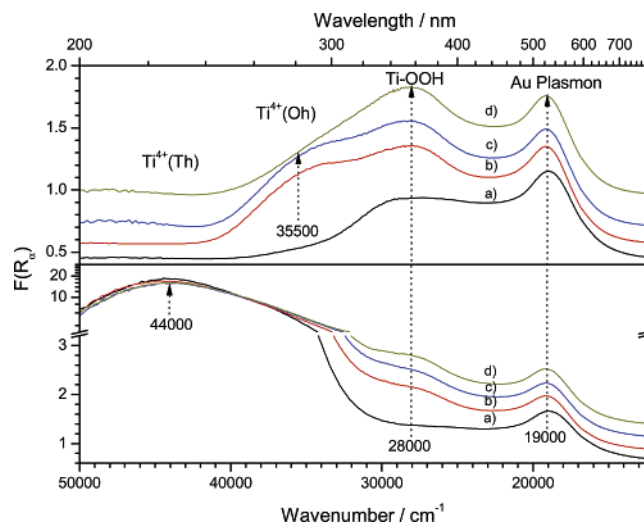


Figure 1. In situ UV-vis spectra for propylene epoxidation on Au/Ti-SiO₂ (Bottom: BaSO₄ referenced, and Top: Ti-SiO₂ referenced): (a) under Ar at 298 K before propylene epoxidation, (b) under C₃H₆/O₂/H₂/Ar (1/1/1/7 in volume) at 423 K for 120 min, (c) under C₃H₆/O₂/H₂/Ar (1/1/1/7 in volume) at 423 K for 270 min, (d) under Ar at 298 K after propylene epoxidation. Offsets are used for clarity.

have been proposed: (1) the formation of hexacoordinated species with two water molecules in the coordination sphere;³⁰ (2) the formation of partly aggregated hexacoordinated species, Ti–O–Ti;^{26–28} and (3) the formation of isolated single-bonded TiO_x species attached to the zeolite lattice.²⁹ The second and third options can be ruled out since no such type of species was found in our earlier study.¹¹ It is also important to point out that in order to act as a catalytic site, the Ti⁴⁺ has to interact with reactants. During adsorption of reactants, Ti⁴⁺ should increase its coordination number, moving from the original tetrahedral framework position to another more external and relaxed in which the Si–O–Ti bonds will be more polarized and elongated with respect to the normal values.²⁰ Using experimental and theoretical calculations, de la Peña O'shea et al.³⁰ showed that hydrated tetrahedral Ti⁴⁺ sites formed new transition bands at wavenumbers higher than 33 000 cm⁻¹ (300 nm). In fact, when a Ti-SiO₂ (Ti/Si = 3:100) sample was contacted with liquid water, a new band arose around 34 100 cm⁻¹ (293 nm) as a result of the water interaction with the tetrahedral Ti⁴⁺ sites. Similarly, in situ experiments in which a sample of Au/Ti-SiO₂ was treated at 423 K with Ar containing H₂O yielded a weak band around 35 000 cm⁻¹ (286 nm) (see Supporting Information). From these experiments, bands characteristic of hydroperoxo species were not observed. We therefore conclude that the band around 35 500 cm⁻¹ (282 nm) appears due to an increase in the Ti⁴⁺ coordination by the formation of complexes with reactants and water molecules, and that H₂O₂ is required for the formation of hydroperoxo species.

Interestingly, the bands in the 26 000–33 000 cm⁻¹ (385–303 nm) region did not appear when the measurements were carried out only on the titanosilicate support alone in the gas phase containing C₃H₆, O₂, H₂, and Ar (1:1:1:7 in volume) at 423 K (see Supporting Information). This observation strongly emphasizes the role of gold species on the hydroperoxo species formation and PO production, supporting our proposal that the presence of gold initiates the formation of hydrogen peroxide species from O₂ and H₂ followed by the formation of Ti hydroperoxo species, which is likely to act as an active intermediate for the propylene epoxidation reaction.¹²

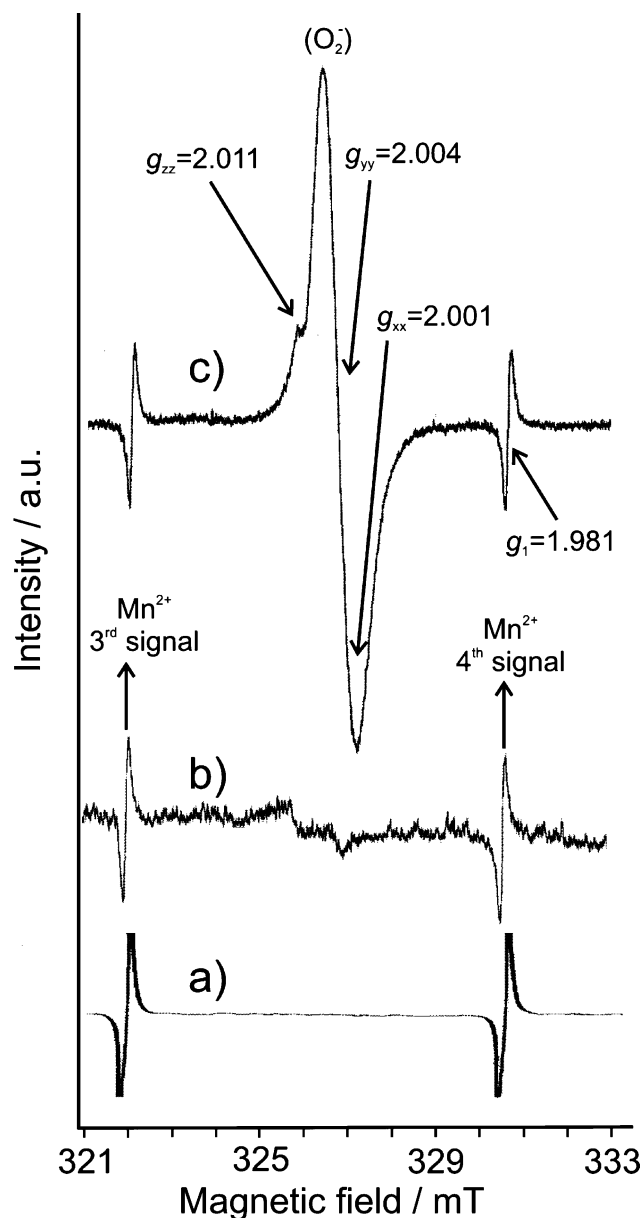


Figure 2. EPR spectra showing the role of gold on the formation of paramagnetic peroxo species on Au/Ti-SiO₂ catalyst surface: (a) Au/Ti-SiO₂ fresh sample before propylene epoxidation, (b) Ti-SiO₂ after propylene epoxidation under C₃H₆/O₂/H₂/Ar (1/1/1/7 in volume) for 270 min, (c) Au/Ti-SiO₂ after propylene epoxidation under C₃H₆/O₂/H₂/Ar (1/1/1/7 in volume) for 270 min. Mn²⁺ is used as an internal standard.

More precise information shedding light on the intermediate species generated on the catalyst surface during the formation of PO can be obtained from EPR measurements. As revealed in earlier studies, O₂ and H₂ interact to produce H₂O₂ over the gold surfaces.^{31,32} Recent DFT calculations for the gas-phase reaction of O₂ and H₂ on gold clusters have suggested the adsorption of O₂ on gold as an intermediate step toward the formation of H₂O₂.³³ In this work it was assumed that intermediate (O₂⁻) species, which is paramagnetic and EPR active, could be trapped and probably adsorbed on the synergetic Au and Ti⁴⁺ sites in the Au/Ti-SiO₂ catalyst. In Figure 2 a new sharp EPR signal attributable to (O₂⁻) with one unpaired electron^{34,35} is observed for the samples after propylene epoxidation, whereas no EPR signals were observed for samples before reaction. In the Au/Ti-SiO₂ catalyst it is difficult to isolate g_x and g_y (2.004),³⁴ but a shoulder due to g_z was observed

at $g = 2.011$. The g_z value of the superoxo anion is sensitive not only to the oxidation state and coordination number but also to the local geometry of the cation to which it is coordinated.¹⁴ The lack of an EPR peak attributable to Ti³⁺ indicates that (O₂⁻) resides on Au, Ti⁴⁺, or more likely at the Au-Ti⁴⁺ interface.³¹ It can also be noted from Figure 2 that no paramagnetic species was formed for the support alone after reaction, which is in accordance with the UV-vis observations. The formation of paramagnetic species can be explained as follows: Au facilitates the formation of this (O₂⁻) species, which during the trapping procedure can spill over to Ti⁴⁺ sites to form superoxo-adsorbed species. Under reaction conditions, Ti-hydroperoxo species can be formed by the transfer of H₂O₂ from the gold surfaces to Ti⁴⁺ sites. In the present work, the presence of oxidic gold along with metallic gold on the freshly prepared and calcined Au/Ti-SiO₂ catalyst was proved by ex-situ XANES (X-ray absorption near edge structure) spectroscopy (see Supporting Information). Miller et al.³⁶ by means of EXAFS and XANES spectroscopies have reported that Au^{III} can be formed along with (O₂⁻) from the interaction of oxygen and metallic gold on small nanoparticles. However, under reaction conditions, i.e., CO oxidation with O₂, Au^{III} is readily reduced and little oxidic Au was observed.^{37,38} Although in the present study in situ XANES spectroscopic measurements during propylene epoxidation were not carried out, from the EPR measurements and the results reported by Miller et al.³⁶ it could be suggested that a little amount of oxidic gold may be present during propylene epoxidation reaction, which could facilitate the adsorption of oxygen as (O₂⁻).³⁹

To confirm the active role of gold nanoparticles supported on titanasilicate materials we have also carried out in situ UV-vis studies on a Au/TS-1 (nominal Au loading ≈ 4.9 wt %, Ti/Si = 1:100) catalyst under similar PO reaction conditions at 473 K and 1 atm. Initial catalytic activities remain even after 6 h of reaction with a propylene conversion of about 1.2% and a PO selectivity of 98.5%. From the in situ UV-vis experiments a feature similar to that obtained for the Au/Ti-SiO₂ catalyst in the 26 000–33 000 cm⁻¹ (385–303 nm) region was also observed (see Supporting Information). These results evidence the formation of hydroperoxo species on gold catalysts supported not only on meso- but also microporous titanasilicate materials.

An additional experiment was carried out for the propylene epoxidation reaction over a Au/SiO₂ catalyst. Mesoporous SiO₂ support and Au/SiO₂ catalyst were prepared following the preparation methods described by Jansen et al.⁴⁰ and Nijhuis et al.,⁴ respectively. Using reaction conditions similar to those for Au/Ti-SiO₂, reactivity results for Au/SiO₂ after 30 min of reaction were a propylene conversion of 0.2% and a PO selectivity of 19.4% (space time yield = 1.2×10^{-5} mol h⁻¹ gcat⁻¹). A comparison with the activity results for the Au/Ti-SiO₂ catalyst (space time yield = 3.7×10^{-4} mol h⁻¹ gcat⁻¹) clearly shows that under these reaction conditions there is only a small contribution to the formation of PO over gold sites and therefore it could be fairly assumed that most of the PO is being formed from the reaction between propylene and the hydroperoxo species on Ti sites. Proving that this hydroperoxo (or adsorbed (O₂⁻)) species is a true intermediate and not a spectator one would require, for example, in situ transient kinetic spectroscopic experiments^{41,42} that are beyond the scope of the present communication.

Propylene epoxidation in gas-phase using O₂ and H₂ was first reported by Hayashi et al.³ using a Au/TiO₂ catalyst at temperatures below 373 K. Despite being highly selective, this catalytic system deactivates quite fast after 1–2 h depending

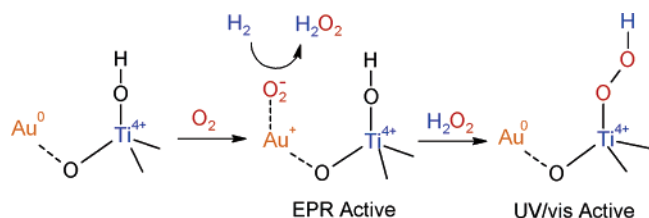


Figure 3. Possible mechanistic model for the formation of hydroperoxo species on Au/titanosilicate materials.

on the reaction temperature.⁴³ Nijhuis et al.^{4,43} have proposed a reaction mechanism for propylene epoxidation on Au/TiO₂ catalyst consisting of two main steps: (1) formation of peroxide species on gold nanoparticles and; (2) formation of bidentate propoxy species from adsorption of propylene on titania sites near gold. Peroxide species react with bidentate propoxy species to form PO and reoxidize the titania sites. These authors did not detect any peroxy species by means of in situ Raman experiments. We have prepared a Au/TiO₂ catalyst (Au 1.2 wt %) by the DP method and carried out in situ UV–vis experiments under similar gas concentrations at 343 K during 2 h of reaction and did not detect any peroxy species either. These results suggest that the reaction mechanisms on Au/TiO₂ and on Au/Ti–SiO₂ materials may proceed in a different fashion, and the formation of hydroperoxo species on tetrahedral Ti⁴⁺ sites in titanosilicate materials is perhaps one of the fundamental differences.

Based on experimental results and literature reports, a mechanistic model for the formation of superoxo/hydroperoxo species on gold supported titanosilicate catalysts is depicted in Figure 3.^{3,12,31} The potential ability of Au to form peroxy type species has been postulated and experimentally verified.^{21,44–46} In this model, gold can activate oxygen and hydrogen to form H₂O₂ via formation of an intermediate (O₂[−]) paramagnetic species on the gold surface.^{33,47} Hydroperoxo species can then be formed by transfer of H₂O₂ to Ti⁴⁺ sites. This hydroperoxo species on the tetrahedrally coordinated Ti cation sites can then react with propylene adsorbed on SiO₂ surfaces to form PO.⁴⁸ The UV active Ti-hydroperoxo species and the EPR active (O₂[−]) species could be directly detected in our experiments. The appearance of both species in appreciable amounts when gold is present highlights the vital role of gold nanoparticles on Ti-hydroperoxo species formation, which are indispensable for the production of PO from propylene.

In conclusion, this study represents the first report for the in situ gas phase formation of superoxo/hydroperoxo species on titanosilicates supported gold nanoparticles highly active for propylene epoxidation. The EPR results give more insight into the steps for Ti-hydroperoxo/peroxo and superoxo species formation supporting previously described in situ UV–vis measurements. EPR detected (O₂[−]) species may be stabilized on small amounts of oxidic Au on the gold surface of the catalyst, probably at the perimeter sites. This direct evidence for peroxo/hydroperoxide species formation on supported gold catalysts contributes to a better understanding of the reaction mechanism of selective oxidation reactions catalyzed by gold supported on Ti–SiO₂ materials.

Acknowledgment. Our sincere thanks to Professor S. T. Oyama for his critical comments and valuable discussion. We are also grateful to Dr. S. Kutsuna for his help with EPR measurements. B.C. acknowledges the financial assistance from AIST, and the governing body of Uluberia College, West Bengal, India for granting special study leave to carry out this

work. J.J.B.-S. gratefully acknowledges the financial support from the Japan Society for the Promotion of Science (JSPS) through the Postdoctoral Fellowships for Foreign Researchers Program (No. P05627). The XAFS experiments were conducted at Photon Factory, Institute for Material Structure Science, High Energy Accelerator Research Organization with the approval of PF-PAC (Project 2004G304).

Supporting Information Available: (1) Cell-reactor for EPR measurements; (2) UV–vis results for Ti–SiO₂ and Au/Ti–SiO₂ contacted with 35% liquid H₂O₂, and water and Ar/H₂O, respectively; (3) XANES spectra showing the presence of oxidic gold in a fresh Au/Ti–SiO₂ catalyst; (4) In situ UV–vis difference spectra results for propylene epoxidation on Au/TS-1 and Au/Ti–SiO₂. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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