Heterogeneous Catalysis

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Propene Epoxidation with Dioxygen Catalyzed by Gold Clusters**

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There are two major shifts that the chemical industry is going to take in the 21st century: a gradual shift to renewable biomass resources and a shift to reactions which produce little waste. After polymerization, the oxidation of hydrocarbons represents the second largest contributor to the total product value in the chemical industry (18 %).[1] The products, functional organic compounds containing oxygen, such as epoxides, ketones, aldehydes, alcohols, and acids, are used for producing polymers, surfactants, detergents, cosmetics, and other products. If the selective oxidation of hydrocarbons could be efficiently carried out by using dioxygen (O_2) or air alone instead of using oxidants, such as hazardous chlorine or costly organic peroxides, it would contribute to the conversion of current chemical production into a green and sustainable industry.

In particular, if the selective oxidation of propene (C_3H_6) with O_2 to propene epoxide (PO) was realized, it might spark considerable technological innovation in the chemical industry. Indeed, this reaction has been regarded as the Holy Grail in catalysis research[2] because a huge energy of 497 $kJ\,mol^{-1}$ is needed to dissociate O_2 (Figure S1 in the Supporting Information)[3] and, once atomically dissociated, oxygen tends to be negatively charged (O^-), and preferentially attacks the weakly bound allylic hydrogen atoms ($-CH_3$) in propene resulting in the production of acrolein (Figure S2 in the Supporting Information).

Propene epoxide is an important bulk chemical which is used for producing mainly polyurethane foams and resins, and propylene glycol. Its annual worldwide production has grown at a rate above 4.0 % and amounted to approximately 7.5 million tons in 2007.[4] Propene epoxide is currently produced by the chlorohydrin process and several organic peroxide processes.[5] The chlorohydrin process is accompanied by the by-production of $CaCl_2$ (2.2 tons per 1.0 ton of propene epoxide) together with toxic chlorinated organic compounds (several hundreds grams per 1.0 ton propene epoxide), whereas the organic peroxide processes usually suffer from the mismatch of market demand for the products, because the demand for the co-products, such as *tert*-butyl alcohol and styrene, is less than for propene epoxide. Recently two new processes have been developed: a cumene hydroperoxide process in 2003[6] in Japan where the co-product, cumyl alcohol, is recycled by reduction with hydrogen (H_2); and a hydrogen peroxide (H_2O_2) epoxidation process in 2008[7] in Belgium using methanol as a solvent. However, these new industrial processes are still based on multi-staged liquid-phase reactions and require hydrogen.

In contrast to the simple industrial process for the gas-phase epoxidation of symmetrical ethene (C_2H_4) with dioxygen over a silver (Ag) catalyst, the use of silver catalysts in propene epoxidation with O_2 usually resulted in propene epoxide selectivities of less than 50 %,[8,9] while gold (Au) sponge or Au/SiO_2 was reported to yield acrolein as a main product but no propene epoxide.[10] An alternative route which needs no substantial energy is the reductive activation of O_2 with H_2 (5.9 $kJ\,mol^{-1}$, Figure S1 in the Supporting Information) under milder conditions. This process can be regarded as an in situ H_2O_2 synthesis process. One of us reported in 1998 the gas-phase C_3H_6 epoxidation with O_2 and H_2 mixture over gold nanoparticles (NPs, 2.0–5.0 nm) deposited on anatase TiO_2.[11] Since then, the catalytic performances have been appreciably improved by optimizing catalyst formulations.[12–14] For example, gold nanoparticles deposited on mesoporous titanium-silicate present a propene epoxide selectivity of 91 % at a C_3H_6 conversion of 8.5 %.[12]

Herein, gold clusters with diameters below 2.0 nm were deposited on alkaline-treated titanosilicalite-1 (TS-1) by solid grinding (SG) with dimethyl gold(III) acetylacetonate.[15] These gold-cluster catalysts exhibited, without any promoters, high stability (for more than 24 h) as well as high catalytic activity (C_3H_6 conversion about 8.8 %) and propene epoxide selectivities (about 82 %) in C_3H_6 epoxidation with an $O_2 + H_2$ mixture. Over 0.19 wt % Au/TS-1-K1 (herein alkaline-treated TS-1 is denoted as TS-1-K1, where K stands for KOH and 1 stands for 1.0 h, see Experimental Section for the preparation of TS-1-K1) with a mean gold diameter of 1.8 nm, a small amount of propene epoxide is produced even from a mixture of C_3H_6 and O_2 (Table S1 in the Supporting

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Information). The addition of H_2O vapor to the feed gas markedly enhanced the catalytic performance to a C_3H_6 conversion of 0.88% and a propene epoxide selectivity of 52% (Table 1). In contrast, over 0.19 wt% Au/TS-1 (without alkaline treatment) prepared by the solid-grinding method, only large gold particles were observed with a mean diameter of 4.6 nm and no propene epoxide was formed even when H_2O vapor was introduced to the feed gas (Table 1). Since elemental analyses showed that both gold catalysts had identical actual gold loading and Ti content, and a very similar potassium content (Table S2 in the Supporting Information), the main difference in propene epoxide production could be ascribed to the difference in the diameter of gold particles.

We further used TS-1 treated with NaOH or CsOH instead of KOH as a support and deposited gold clusters over them by solid grinding or deposition–precipitation (DP). These gold/alkaline treated TS-1 could also catalyze C_3H_6 epoxidation with O_2 in the presence of H_2O, while catalytic activity, selectivity, or stability was slightly inferior to that over 0.19 wt% Au/TS-1-K1.

In C_3H_6 epoxidation with O_2 alone, two key conditions appear to be of critical importance: isolated Ti sites and gold clusters smaller than 2.0 nm. To find out whether isolated Ti sites are needed or not, γ-Al_2O_3 (specific surface area (SA): 178 $m^2 g^{-1}$), amorphous Al_2O_3 (SA: 193 $m^2 g^{-1}$), TiO_2 (P-25, SA: 46 $m^2 g^{-1}$), and nanoporous carbon (NPC, SA: 577 $m^2 g^{-1}$) were selected as supports. Except for TiO_2, on which the DP method could deposit smaller gold nanoparticles and even gold clusters, the SG method was used to deposit gold as nanoparticles and clusters. To confirm the presence of gold clusters (< 2.0 nm), high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) observation was also carried out. The mean diameter of the gold particles ranged from 1.8 to 2.9 nm. It has recently been reported that Au_{6-10} clusters supported on amorphous Al_2O_3[16] and gold nanoparticles supported on TiO_2[17] can catalyze epoxidation of C_3H_6 with $O_2 + H_2O$. In our experiments no propene epoxide but acrolein and/or CO_2 were produced over gold clusters smaller than 2.0 nm in diameter on titanium-free supports, on TiO_2, and over gold nanoparticles (> 2.0 nm) on TiO_2 (Table 1), indicating that isolated Ti sites are indispensable for gold clusters (< 2.0 nm) to catalyze C_3H_6 epoxidation with $O_2 + H_2O$.

Lambert et al. have recently reported that even on inert support materials, such as silicon dioxide (SiO_2) and boron nitride (BN), the well-defined size control of gold clusters leads to the epoxidation of styrene with selectivity around 30%.[18] The diameter of gold particles is tunable by choosing the calcination temperature for the gold catalysts according to theoretical calculations[19] and experimental results.[20] After propene oxidation reaction, the gold catalysts were examined with HAADF-STEM. Different mean gold nanoparticle diameters of 1.8 nm, 2.0 nm, and 3.5 nm were obtained by controlled calcination at different temperatures (423 K, 573 K, and 673 K, respectively; Table S3 in the Supporting Information). HAADF-STEM images showed that before reaction, 92% of gold particles over 0.19 wt% Au/TS-1-K1 calcined at 423 K (with mean gold particle diameter of 1.6 nm) existed as clusters smaller than 2.0 nm and only a small number of gold nanoparticles were observed between 2.0–4.5 nm (Figure 1 a,c). After reaction at 473 K (Catalyst 1, Table S3 in the Supporting Information), although the mean diameter of the gold species slightly increased to 1.8 nm and some gold nanoparticles larger than 5.0 nm appeared, 87% of gold particles still existed as clusters (< 2.0 nm; Figure 1 b,d). After calcination of 0.19 wt% Au/TS-1-K1 at 573 K (Catalyst 3, Table S3 in the Supporting Information), the mean diameter of gold particles increased to 2.0 nm, while 70% of them were still present as clusters. The catalytic performance of Catalyst 3 was depressed only slightly in comparison with Catalyst 1 (Table S3 in the Supporting Information). However, when calcined at 673 K (Catalyst 4, Table S3 in the Supporting Information), 86% of the gold particles grew to be nanoparticles (> 2.0 nm) with mean diameter of 3.5 nm, and only small amounts of gold clusters remained. The fact that Catalyst 4 produced only a little propene epoxide indicates that gold clusters but not gold nanoparticles were responsible for propene epoxide synthesis. Over Catalyst 5 calcined at 773 K (Table S3 in the Supporting Information), no propene epoxide was produced.

Table 1: C_3H_6 reaction with O_2 in the presence of H_2O over supported gold catalysts.[a]

	Support	Au loading [wt%][b]	Prep. method	Pretreatment atmosphere,[c] temperature [K]	Mean Au particle diameter [nm][d]	Conv. of C_3H_6 [%]	Selectivity [%] propene epoxide	acrolein	CO_2
titano-silicalite	TS-1	0.19	SG	H_2, 423	4.6	0.07	0	34	66
	TS-1-K1	0.19	SG	H_2, 423	1.8	0.88	52	12	36
	TS-1-K1	9.0[e]	DP	H_2, 473	–	0.47	57	7	36
metal oxides	γ-Al_2O_3	0.86	SG	air, 573	2.6	0.15	0	41	44
	Al_2O_3 (amorphous)	0.19	SG	H_2, 423	< 2.0[f]	0.15	0	54	46
	TiO_2	1.2	DP	air, 573	2.9[f]	0.03	0	0	100
	TiO_2	0.10	DP	air, 573	1.8[11]	0.05	0	0	100
carbon	nanoporous carbon	1.0	SG	air, 573	1.9	0.48	0	41	59

[a] Reaction conditions: catalyst 0.30 g; reaction temperature 473 K (for Au/TiO_2, 353 K); feed gas $C_3H_6/O_2/H_2O/Ar = 10/10/2/78$; space velocity 4000 $mL\,g^{-1}_{cat.}\,h^{-1}$. Data were taken under a steady state after at least 2.0 h duration. [b] Actual Au loadings obtained by inductively coupled plasma (ICP) analysis. [c] H_2 (10 vol%) was diluted by 90 vol% Ar. [d] The diameters of gold nanoparticles or clusters determined by HAADF-STEM observation after catalytic tests. [e] Gold loading calculated from the gold content in the starting solution. [f] The diameters of gold nanoparticles or clusters determined by TEM observation after catalytic tests. Over Au/amorphous Al_2O_3, because no Au particles could be found by TEM, the diameter was estimated to be smaller than 2.0 nm. SG = solid grinding, DP = deposition–precipitation.

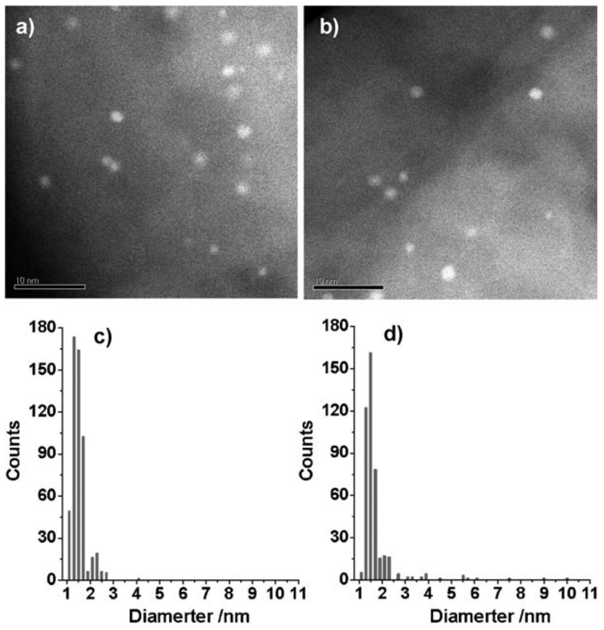


Figure 1. a,b) HAADF-STEM images and c,d) diameter distribution of gold particles (c: 535, d: 436 counts) for 0.19 wt% Au/TS-1-K1. (a,c): before reaction of samples reduced in 10 vol% H_2 balanced with Ar at 423 K; (b,d): after reaction for 21 h of samples reduced under the same conditions as in (a,c). Reaction conditions: catalyst 0.30 g; reaction temperature 473 K; feed gas $C_3H_6/O_2/H_2O/Ar = 10/10/2/78$; space velocity 4000 mL $g^{-1}_{cat.}$ h^{-1} (scale bar: 10 nm).

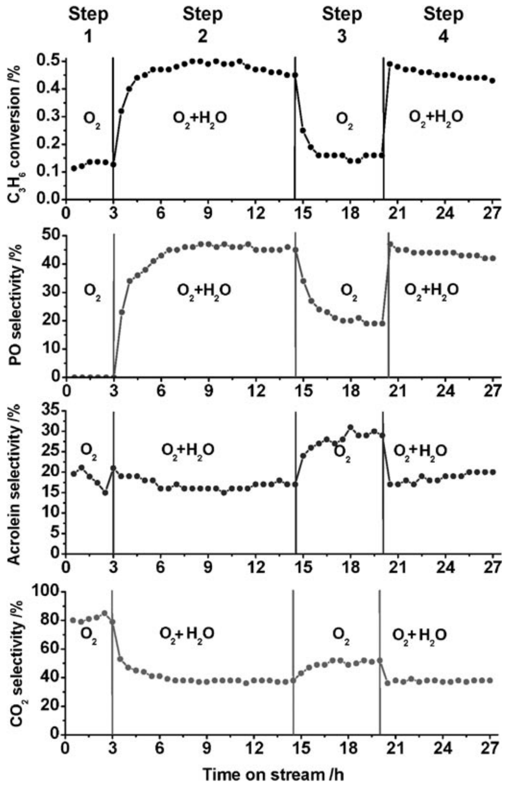


Figure 2. Enhancing effect of H_2O on propene epoxidation with O_2 over 0.10 wt% Au/TS-1-K1. Reaction conditions: catalyst 0.30 g; reaction temperature 473 K; feed gas $C_3H_6/O_2/Ar = 10/10/80$ or $C_3H_6/O_2/H_2O/Ar = 10/10/2/78$; space velocity 4000 mL $g^{-1}_{cat.}$ h^{-1}. Step 1: without H_2O; Step 2: H_2O was added to the feed gas; Step 3: the addition of H_2O was stopped; Step 4: H_2O was added to the feed gas again.

To investigate the promoting effect of H_2O, Au/TS-1-K1 with a lower gold loading of 0.10 wt% was used, because H_2O can be produced in situ if C_3H_6 is oxidized to acrolein or CO_2. No propene epoxide was produced when only O_2 was supplied to the feed gas of C_3H_6 in Figure 2, Step 1. The addition of H_2O to the feed gas enhanced the formation of propene epoxide to a selectivity of about 47% as well as the conversion of C_3H_6 (Figure 2, Step 2). Since H_2O was not consumed and no product from H_2O decomposition, such as H_2, was detected, H_2O can be regarded as a gas-phase promoter. When H_2O was removed from the feed gas, propene epoxide selectivity decreased quickly from 45% to only 20% with an appreciably depressed C_3H_6 conversion of about 0.15% (Figure 2, Step 3). The small amount of propene epoxide formed can be ascribed to H_2O physically adsorbed in Step 2 and to H_2O produced in situ. When H_2O was introduced to the feed gas again (Figure 2, Step 4), both propene epoxide selectivity and C_3H_6 conversion were recovered to the levels of Step 2 (Figure 2).

To answer the question of why H_2O can enhance C_3H_6 epoxidation with O_2 over Au/TS-1-K1 (Figure 2), in situ UV/Vis spectroscopy was used to monitor this reaction. Before in situ monitoring, UV/Vis spectra of TS-1-K1 were obtained after contact with liquid H_2O or aqueous H_2O_2 (Figure S3 in the Supporting Information). The spectrum after contact with liquid H_2O displayed a shoulder peak centered at 265 nm,[21] and the spectrum after contact with aqueous H_2O_2 showed a broad band at 300–450 nm.[22] The difference spectra obtained in a stream of O_2 and H_2O (Figure S4 in the Supporting Information) showed that a band at 255 nm ascribed to H_2O adsorption and a band at 333 nm directly related to Ti-OOH species[23] appeared, indicating the formation of hydroperoxides from O_2 and H_2O. As shown in Figure 3, the intensity of this band gradually increased with time on stream until about 100 min and then leveled off. The addition of C_3H_6 to the feed gas resulted in a gradual decrease in the intensity of this band, suggesting that Ti-OOH species were consumed by C_3H_6 and this happened more quickly than the formation of Ti-OOH species. Once water was removed from the feed gas, the band intensity of the Ti-OOH species quickly decreased, which strongly indicates that H_2O was indeed required for the formation of the Ti-OOH species.

As described above, Ti-OOH species can be formed over Au/TS-1-K1 directly from $O_2 + H_2O$. However, if only TS-1-K1 without gold clusters was monitored by in situ UV/Vis spectroscopy, no Ti-OOH species could be detected, meaning that gold clusters are indispensable for the formation of hydroperoxides (-OOH species). Theoretical calculations also confirmed that over gold clusters, hydroperoxides can be produced directly from $O_2 + H_2O$.[24] Scheme 1 illustrates a possible epoxidation route. First, O_2 reacts with H_2O over gold cluster surfaces to produce -OOH species. Then -OOH species reversibly transfer from gold cluster surfaces to neighboring Ti sites to form Ti-OOH species, which are responsible for subsequent C_3H_6 epoxidation. It is likely that during the reaction $O^{\bullet}$ radicals would be produced and further

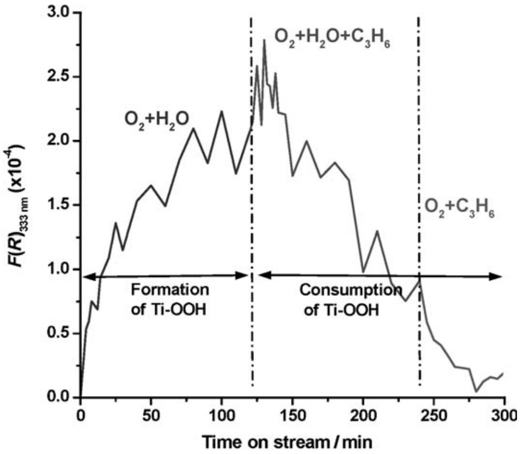
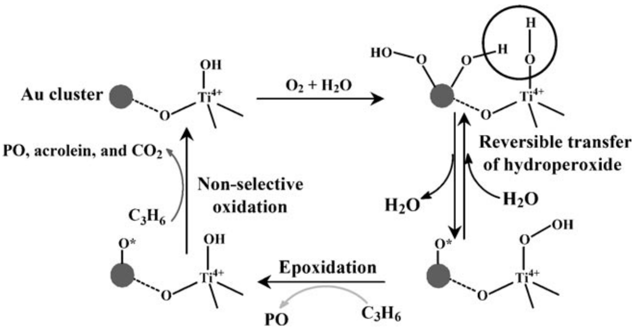


Figure 3. Intensity of in situ UV/Vis peak at 333 nm (assigned to Ti-OOH) under different feed-gas compositions over 0.19 wt% Au/TS-1-K1. After the catalyst sample was kept in Ar at 473 K for 1.0 h (reference spectrum was taken), the feed gas was switched to O_2+H_2O mixture ($O_2/H_2O/Ar=10/2/88$), and then after 2.0 h, C_3H_6 was added ($C_3H_6/O_2/H_2O/Ar=10/10/2/78$). After another 2.0 h, H_2O was removed from the feed gas. Reaction conditions: catalyst about 40 mg; reaction temperature 473 K; rate of flow 20 mL min^{-1}; space velocity 30000 mL g$^{-1}_{cat.}$ h^{-1}.



Scheme 1. A possible route for C_3H_6 epoxidation with O_2+H_2O over Au/TS-1-K1. PO = propene epoxide.

used to oxidize C_3H_6 to propene epoxide, acrolein, and CO_2. Accordingly, propene epoxide selectivity can be improved by controlling the reactivity of O$^•$ radicals over the surfaces of gold clusters.

In conclusion, the gas-phase epoxidation of propene with dioxygen can be catalyzed, in the presence of H_2O, by gold clusters (< 2.0 nm) deposited on alkaline treated TS-1. The metal time yield of propene epoxide was 2.3 $g_{PO}\,g^{-1}_{Au}\,h^{-1}$ with propene conversion near 1.0% and propene epoxide selectivity above 50%. Although this performance is not sufficiently high for an industrial application, it is better than those of copper- and silver-based catalysts reported to date (Figure S5 and Table S4 in the Supporting Information). Therefore, our gold-based catalysts have greater potential for future improvement if the size of the gold clusters, the configuration of the gold clusters and isolated Ti sites, and the reactivity of the active O$^•$ radicals towards propene epoxide can be optimized. Accordingly, supported gold clusters may be a significant stepping stone towards the development of environmentally friendly chemical processes.

Experimental Section

Alkaline treatment of TS-1: Aqueous solution of 1.0 M KOH (or NaOH or CsOH) was added dropwise to the suspension of TS-1 (1.0 g) in H_2O (100 mL) at 303 K under vigorous stirring until the pH value of the suspension reached 12, it was then kept at 12 for 1.0 h by adding a small amount of aqueous KOH dropwise. The suspension was collected by filtration, washed five times with 2000 mL of H_2O to remove residual KOH and was dried at 373 K overnight. The alkaline-treated TS-1 was denoted as TS-1-K1, where K stands for KOH and 1 stands for 1.0 h.

Deposition of gold nanoparticles and clusters by solid grinding (SG): TS-1, alkaline-treated TS-1, γ-Al_2O_3, amorphous Al_2O_3, and nanoporous carbon (NPC) were used as supports. The powder of TS-1, TS-1-K1, or amorphous Al_2O_3, and dimethyl gold(III) acetylacetonate [$Me_2Au(acac)$] which has a vapor pressure of 1.1 Pa at 298 K were ground in an agate mortar in air for 15 min at room temperature, followed by reduction in a stream of 10 vol% H_2 in Ar at 423 K for 1.0 h. With γ-Al_2O_3 and NPC as supports, the supports and [$Me_2Au(acac)$] were ground by ball milling. [$Me_2Au(acac)$], γ-Al_2O_3, and acetone were ground (350 rpm) at room temperature for 1.0 h, and grinding of NPC was performed (300 rpm) for 5.0 h in the absence of solvent. Final treatment of both gold catalysts was carried out by calcination in air at 573 K for 4.0 h.

Spectroscopic measurements: In situ UV/Vis diffuse reflectance spectra were collected using a large-compartment spectrometer (Varian Cary 5000). About 40 mg of 0.19 wt% Au/TS-1-K1 (reduced in 10 vol% H_2 in Ar at 473 K) was loaded in a reaction chamber (Harrick Scientific, model HVC-DRP) provided with a praying mantis diffuse reflectance attachment (DRP-XXX). Spectra were recorded at 473 K under atmospheric pressure in a stream of the reactant gases at 20 mL min^{-1}. Spectra were taken in the range of 200–800 nm at a scan rate of 600 nm min^{-1}, an averaging time of 0.1 s, and a data interval of 1 nm. Spectra were referenced to 0.19 wt% Au/TS-1-K1 treated at 473 K under Ar just before introduction of O_2+H_2O mixture (difference spectra). The presented spectra were obtained by applying the Kubelka-Munk function, $F(R)$, to the collected absorbance data.

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