Epoxidation Catalysts

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Trimethylamine as a Gas-Phase Promoter: Highly Efficient Epoxidation of Propylene over Supported Gold Catalysts**

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Propylene oxide (PO) is an important bulk chemical for the production of a wide variety of derivatives, among which polyether polyols and propylene glycol are the main end products.[1] The world PO production of about 5 million tons per year comes from two current industrial processes: the chlorohydrin process and the organic hydroperoxide process (Halcon method). These two methods consist of two reaction stages and produce large amounts of by-products and co-products, which makes optimization difficult.[2]

Although bulk gold was for a long time regarded as a poor catalyst, gold nanoparticles (2–5 nm) deposited on a variety of metal oxides are surprisingly active for many reactions.[3] An alternative route for synthesizing PO by reductive activation of O_2 by H_2 over nanoparticulate gold catalysts has been under investigation for the past few years.[4–7] We have estimated that the requirements for a viable industrial process are a propylene conversion of 10 %, a PO selectivity of 90 %, and a H_2 efficiency of 50 % for the H_2O_2 formed in situ for epoxidation purposes. Recently, we reported a trimethylsilylated $Ba(NO_3)_2$-Au/titanosilicate (Ti/Si 3:100) catalyst that thus far exhibits the highest PO yield among the gold catalysts.[8] The main hurdles for the industrial application of this catalyst are its fast deactivation caused by the accumulation of oligomerized and oxidized PO by-products around the gold nanoparticles, the lower activity of the successively regenerated catalyst, and its low H_2 efficiency. Nowadays, the development of catalysts for use on a commercial scale seeks high atom efficiencies of chemical reactions to reduce manufacturing costs and to minimize burdens on the environment. A comparison of different processes shows that the epoxidation with O_2 and H_2 at 90 % PO selectivity and 50 % H_2 efficiency gives an atom efficiency of 50 %, which is close to the 76 % PO selectivity for the epoxidation with O_2 alone (Supporting Information). This clearly demonstrates that, at present, a more feasible and rational path towards higher atom efficiency is the direct epoxidation of propylene with O_2 and H_2.

We now report that the presence of trimethylamine (TMA), a strong Lewis base with a pK_a value of 9.9,[9] at extremely low concentrations (10–20 ppm) in the reactant gas mixture can remarkably improve the catalytic performance of gold nanoparticles deposited on titanosilicate in terms of catalyst lifetime, catalyst regeneration, PO selectivity, and H_2 efficiency to a level where commercial requirements are almost fulfilled. We have previously shown that a small amount of H_2O can act as a gaseous promoter by drastically altering the catalytic activity of supported gold nanoparticles for low-temperature CO oxidation.[10] The concept behind this investigation was that gaseous trimethylamine should have a positive effect on the overall PO catalyst efficiency. One of the assumptions is that TMA can poison the Lewis acidic sites of the support, mainly isolated Ti^{4+} centers. By oligomerization,[11] cracking, and isomerization, these sites form PO by-products that cause catalyst deactivation. Another possible benefit of TMA is that its adsorption on the gold surface can suppress H_2 combustion to produce water, which results in an improved hydrogen efficiency.

The catalyst activity data show that deactivation is appreciably depressed for the trimethylsilylated $Ba(NO_3)_2$-promoted Au/titanosilicate catalyst (Figure 1) in the presence of 13–15 ppm TMA as a gaseous promoter, leading to a more stable propylene conversion. Up to 80 % of the high initial activity of the catalyst remains after 5 h of operation with almost constant PO selectivity and H_2 efficiency. Surprisingly, the catalyst regenerated in the presence of TMA exhibits an improved performance compared to the fresh catalyst as it presents a slightly better propylene conversion, about 4 % higher PO selectivity, and about 15 % higher H_2 efficiency. In a series of experiments we found enhancements in H_2 efficiency with reaction time and in PO selectivity as the concentration of TMA in the feed mixture was increased up to 20 ppm (Supporting Information). We also observed that for different reaction conditions the presence of TMA during pre-treatment and during the reaction led to the best catalyst performance. Ethylene oxide is produced industrially at a steady space–time yield of 0.032–0.32 $g\,h^{-1}\,(cm^3\,cat)^{-1}$ at 10–35 atm.[12] The rate of production of PO in this report is 0.064–0.080 $g\,h^{-1}\,(g\,cat)^{-1}$ (1 g cat = 2.5 cm^3 cat) even when operating at atmospheric pressure, which indicates that the present process comes close to commercial levels.

To investigate the reason behind the improved catalyst performance after regeneration with TMA, UV/Vis/NIR

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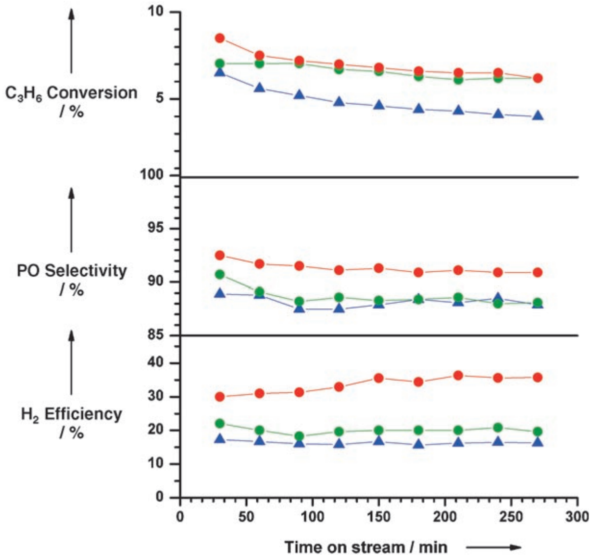

Figure 1. Effect of trimethylamine (13–15 ppm) on the activity of a trimethylsilylated Au-Ba$(NO_3)_2$/titanosilicate (Ti/Si 3:100) catalyst for propylene epoxidation with O_2 and H_2 at 423 K. Reactant gas: C_3H_6/O_2/H_2/Ar = 1:1:1:7; space velocity (SV) = 4000 mL h^{-1} (g cat)$^{-1}$ (PO: propylene oxide); blue ▲: fresh catalyst in the absence of TMA; green ●: fresh catalyst in the presence of TMA; red ●: regenerated catalyst in the presence of TMA.

spectral measurements were carried out in situ. The in situ NIR spectra of the trimethylsilylated Au/titanosilicate catalyst show bands in the region of 6000–5500 cm^{-1} (Figure 2) assigned to the overtones and combination bands of CH_3 groups.[13] This pattern changes when the catalyst is heated in an Ar stream containing 10 vol. % H_2 and 10 vol. % O_2 at 523 K. The bands between 5920 and 5738 cm^{-1} decrease significantly in intensity and the intensity of the silanol bands around 7320 cm^{-1} increases for the untreated gold catalyst (Figure 2, spectra a and b), thereby indicating hydrolysis of –O–Si–O–Si$(CH_3)_3$ groups. Treatment of the silylated gold catalysts with trimethylamine, however, protects the Si–CH_3 bonds in the –O–Si–O–Si$(CH_3)_3$ structure from the destructive effects of moisture, as evidenced by the preservation of the intense bands in the 6000–5500 cm^{-1} range in the NIR spectrum. It is also clear that the intensity increase of the silanol bands is less pronounced for the trimethylamine-treated silylated catalyst than for the catalyst that has only been silylated. These experimental results strongly suggest that the interaction between trimethylamine and the silicon atoms of the silane groups through the nitrogen lone pairs could preserve the Si–CH_3 bonds of the –O–Si–O–Si$(CH_3)_3$ structures in the vigorous reaction environment.[14,15]

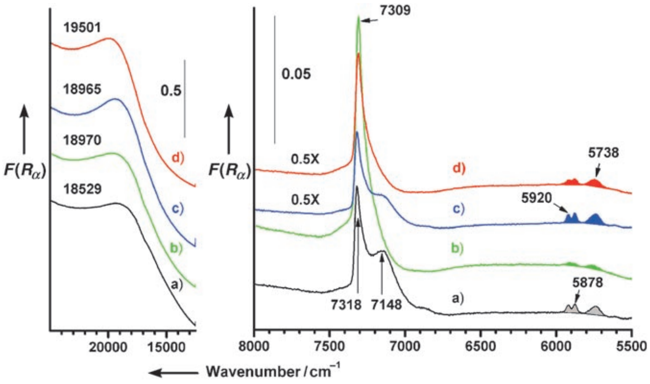

Figure 2. In situ UV/Vis/NIR spectra of trimethylsilylated Au/titanosilicate (Ti/Si 3:100) catalyst: a) in a stream of Ar at 298 K; b) in a stream of O_2, H_2, and Ar at 523 K for 1 h; c) in a stream of Ar at 298 K after treatment in a stream of Ar containing 13–15 ppm TMA at 523 K; d) in a stream of H_2, O_2, and Ar at 523 K for 1 h after treatment in a stream of Ar containing 13–15 ppm TMA at 523 K. Spectra are referenced to $BaSO_4$.

During in situ UV/Vis/NIR measurements attention was also paid to the position of the gold plasmon resonance (Figure 2), which is shown in the case of untreated and TMA-treated trimethylsilylated Au/titanosilicate catalysts during regeneration with O_2 and H_2. In these spectra a single peak, assigned to the plasmon resonance of metallic gold nanoparticles, is observed around 18500–19500 cm^{-1}. Raising the temperature from 298 to 523 K in the presence of O_2 and H_2 gives rise to a slight blue shift in the plasmon resonance peak. This shift may be due to a change in the dielectric constant around the surface of the gold nanoparticles, as described by a multi-layer core–shell model.[16,17] In Figure 2 we compare the spectra at 298 K in argon of the untreated and TMA-treated samples—a blue shift of 436 cm^{-1} is observed (spectra a and c). Similarly, a higher blue shift of 531 cm^{-1} is also found at 523 K in the presence of a mixture of O_2, H_2, and Ar (spectra b and d). These blue shifts after treatment in a stream containing TMA are in good agreement with the depression of H_2 combustion, that is, an increase in H_2 efficiency, and indicate TMA adsorption on the gold surface.

A mechanism for PO formation on the TMA-treated trimethylsilylated Ba$(NO_3)_2$-Au/titanosilicate has been developed that takes into account the present experimental results as well as literature reports (Figure 3). In this process, hydrogen and oxygen react to form H_2O_2 and H_2O over the Au surfaces, thus the H_2 efficiency is usually below 100 %. The potential capacity of Au surfaces to form peroxo species has been predicted and later confirmed experimentally.[18–21] The presence of this oxygen species was proved for propylene epoxidation with H_2O_2 in MeOH solvent over a TS-1 catalyst.[22] Once the H_2O_2 is produced on the gold particles, it can be converted into hydroperoxo species at tetrahedrally coordinated Ti cation sites. These Ti–hydroperoxo species can subsequently react with propylene adsorbed on the SiO_2 surfaces to form PO. In situ UV/Vis measurements of the silylated Au/titanosilicate catalyst during propylene epoxidation (Supporting Information) revealed a broad feature at 29400–23800 cm^{-1} that corresponds to the well-known charge-transfer interaction between a hydroperoxide ligand (OOH^-) and Ti^{4+}.[23] As evidenced by reactivity studies and UV/Vis results, the blue shift in the Au plasmon position suggests that the TMA is partly adsorbed on the Au surfaces and depresses direct H_2O formation. Due to its basic properties, PO should compete strongly with TMA to adsorb on the catalyst surface. Pre-adsorption of TMA on Ti^{4+} can therefore inhibit PO adsorption and its subsequent oligomerization,

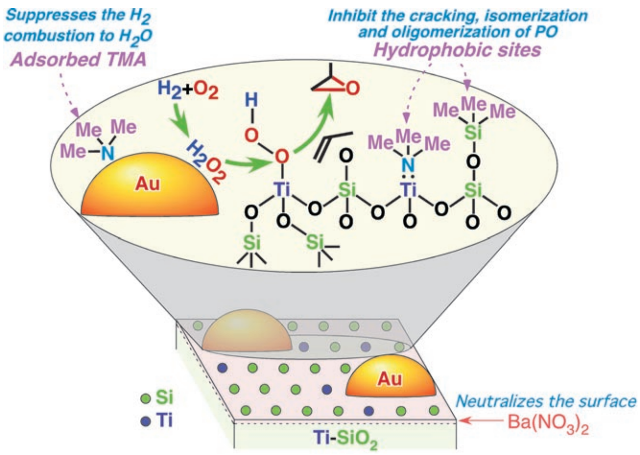

Figure 3. Probable reaction pathways for propylene epoxidation with O_2 and H_2 in the presence of trimethylamine on trimethylsilylated Au-$Ba(NO_3)_2$/titanosilicate catalyst. The accumulation of PO and its derivatives on the catalyst surface can be minimized by changing the surface nature into a hydrophobic one to prevent catalyst deactivation. Hydrogen combustion over Au surfaces can also be suppressed by the adsorption of trimethylamine to improve the atom efficiency of the overall reaction.

which is considered to be one of the main deactivation mechanisms of Au/titanosilicate catalysts.

We therefore conclude that PO can be efficiently produced at around 423 K in the gas phase with propylene, O_2, H_2, and a trace amount (10–20 ppm) of trimethylamine over gold nanoparticles deposited on three-dimensional mesoporous titanosilicates. A steady space–time yield of PO of 1.1–1.4×10^{-3} $\mathrm{mol\,h^{-1}(g\,cat)^{-1}}$ at atmospheric pressure, which is close to that of ethylene oxide in the current industrial process, was achieved for more than 250 min with a propylene conversion up to 8.5 % and a PO selectivity of 91 % under an hourly space velocity of 4000 $\mathrm{mL\,h^{-1}(g\,cat)^{-1}}$. The efficient regeneration of the Au/titanosilicate catalyst using a trace amount of TMA along with a mixture of hydrogen, oxygen, and argon at 523 K, and the improvement of the hydrogen efficiency to 35 %, opens the door to commercialization of this catalytic process. The beneficial role of TMA on the Au/titanosilicate surface was probed by in situ UV/Vis/NIR spectroscopy. This economic synthetic method can be used to produce PO effectively, and is an example of a chemical process that can meet industrial standards while being environmentally benign.

Experimental Section

The titanosilicate support (Ti/Si 3:100) was prepared as reported previously.[8] In a typical preparation of titanosilicate-supported Au catalysts by the DP (deposition–precipitation) method, a solution of $HAuCl_4\cdot4H_2O$ (2 mmol) in water (100 mL) was heated to 343 K, and the pH was adjusted to 7.0 by adding aqueous NaOH solution. The support powder (1.0 g) was dispersed and stirred for 15 min while NaOH solution was added dropwise to maintain the pH at 7.0. Then, $Ba(NO_3)_2$ (0.2 mmol) dissolved in water (5 mL) was added and the mixture was stirred for another 45 min at the same temperature and pH. The solid was collected by filtration, dried under vacuum for 12 h, and then calcined in air at 573 K for 4 h.

The activity of all catalysts was evaluated within 24 h of gold deposition in an effort to minimize any deactivation due to aging. Unless otherwise stated, each fresh catalyst was silylated and then pre-treated with 10 vol. % H_2 in Ar for 30 min followed by 10 vol. % O_2 in Ar for 30 min at 523 K before reaction in a fixed-bed, U-shaped quartz reactor (internal diameter 10 mm). The catalysts were trimethylsilylated at 423 K by passing methoxytrimethylsilane vapor (maintained at 298 K) in an Ar stream over the catalyst for 30 min, followed by flushing with Ar at 473 K (5 h). Then, a feed of propylene, O_2, H_2, and Ar (1:1:1:7 volume ratio) was passed through the catalyst bed at 423 K. Argon containing 5–45 ppm TMA was used as a base gas while studying the effect of TMA on propylene epoxidation. The feed and products were analyzed with on-line GCs equipped with a TCD (Porapak Q column), a FID (HR-20M column), and an auto injector.

In situ UV/Vis/NIR 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). Spectra of catalysts and reference ($BaSO_4$ and titanosilicate support) were recorded under the same reaction and regeneration conditions in the range 200–2500 nm (50000–4000 $\mathrm{cm^{-1}}$). Catalyst samples were pre-treated with TMA in the original reaction line in a similar manner to that of the catalytic activity measurements, then cooled to room temperature, and transferred into the in situ UV/Vis/NIR reaction chamber.

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