**Epoxidation of Propene**

# A Three-Dimensional Mesoporous Titanosilicate Support for Gold Nanoparticles: Vapor-Phase Epoxidation of Propene with High Conversion**

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Gold nanoparticles deposited on $TiO_2$[1] provide a new route for the direct epoxidation of propene using molecular oxygen. Such an alternative direct gas-phase epoxidation process is of tremendous industrial significance and is more environmentally friendly than the multistep chlorohydrin and hydroperoxide processes that are currently employed.[2] We have established the viability of the vapor-phase epoxidation of propene over nanosize Au catalysts supported on Ti-containing supports such as $TiO_2$, $TiO_2/SiO_2$, TS-1, Ti-MCM-41, Ti-MCM-48, and Ti-containing hydrophobic silsequioxanes.[3–10] However, low conversion of propene, rapid catalyst deactivation, and regeneration problems have all been major hurdles in making the process commercially viable, even though propene oxide (PO) selectivity is greater than 90 %. Based on a rough estimate for the commercialization of vapor-phase propylene epoxidation with $H_2$ and $O_2$, we set the following research targets: one-pass propylene conversion of 10 %, PO selectivity of 90 %, and hydrogen efficiency of 50 %.

A new class of disordered mesoporous materials with channels of uniform width interconnected in a three-dimensional (3D) wormholelike fashion[11] have the advantage over their more ordered counterparts such as MCM-41 of better diffusion of reactants and products and thus overcome mass-transfer limitations. Furthermore, their higher thermal stability and cheap, easy, and reproducible preparation make these materials more suitable for industrial applications. The possibility to tailor their porosity (between 5 and 10 nm)[12] makes the mesopores easily accessible for a dispersion of 2–5 nm Au particles by the deposition–precipitation (DP) method,[1] in contrast to the narrower pores (3–4 nm) of MCM-type supports, for which access to the mesopores by Au nanoparticles is limited.

Here we demonstrate for the first time that it is possible to prepare a commercially viable Au catalyst for the direct

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epoxidation of propene. The catalyst is a high-Ti (3–6 mol%) 3D mesoporous silylated titanosilicate in which Au nanoparticles are dispersed on the surface and in the mesopores, and its activity is further promoted by an alkaline-earth-metal nitrate promoter. Our intention was to exploit the advantages of large-pore, 3D wormholelike mesoporous titanosilicates as supports for nanosized gold catalysts in the direct epoxidation of propene to PO with molecular oxygen. Moreover, it is possible to enhance the hydrophobicity of these titanosilicates by trimethylsilylation of the silanol sites, which is expected to enhance PO desorption and hence PO yield and also to slow down the deactivation of the catalyst. Furthermore, addition of certain metal salts as promoters can enhance the performance of the catalyst.

The X-ray powder diffraction patterns (Figure 1 a) of calcined titanosilicate materials show a broad peak around $2\theta = 1.0$–$2.0°$, which is typical for disordered mesostructured materials. Such XRD patterns are similar to those of mesostructured MSU-1,[11] UTD-1,[12] HMS,[13] and KIT-1,[14] which have 3D networks of short, interconnected, wormholelike mesopores. High-resolution TEM images (Figure 1 a, inset) confirmed the presence of such uniform, 3D networks of short interconnected wormholelike channels. The diffuse-reflectance UV spectra (Figure 1 b) show that samples with Ti concentrations of up to 6.0 mol% exhibit absorbance peaks at 220–245 nm, which result from tetrahedrally coordinated Ti centers, that is, most of the titanium is present as isolated tetrahedral species in the silica matrix. The samples yielded no peaks above 300 nm, which indicates the absence of any bulk titania. The sample with the highest titanium concentration (8 mol%) shows two clear peaks, one at 235 nm due to tetrahedrally coordinated titanium, and another at 272 nm, attributable to higher (5-, 6-) coordinate Ti. The XPS analysis of titanosilicates with 2–6 mol% titanium content showed that the binding energy (BE) of the Ti $2p_{3/2}$ core level is about 460.0 eV, which indicates tetrahedral coordination of completely isolated Ti sites in the silica lattice.[15] However, the shift of the BE to 459.3 eV at higher Ti content (8 mol%) indicates incomplete isolation of Ti sites for high Ti content.[16] The BE is about 458.5 eV for aggregated Ti with octahedral coordination.[16] The BET surface area, Barrett–Joyner–Halenda (BJH) pore diameter, and mesopore volume were 838–896 $m^2g^{-1}$, 7.1–9.2 nm, and 1.0–1.4 $cm^3g^{-1}$, respectively.

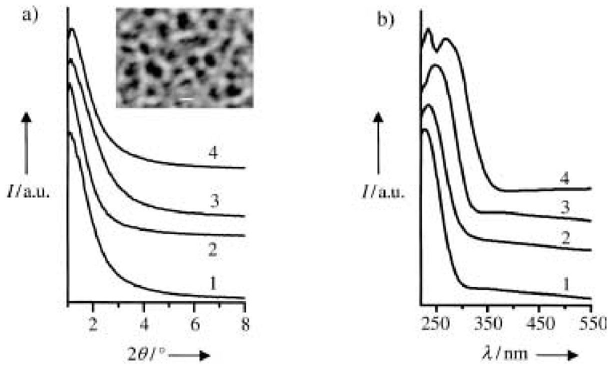

**Figure 1.** a) XRD spectra (inset: high-resolution TEM image; 3% Ti; scale bar = 6 nm), and b) diffuse-reflectance UV/Vis spectra of 3D mesoporous titanosilicates. Titanium concentrations: 1) 2.0 mol%, 2) 3.0 mol%, 3) 6.0 mol%, 4) 8.0 mol%. I = intensity.

Gold nanoparticles were deposited on all the supports by the DP method. The gold loading on the resultant materials was 0.3–0.4 wt%, and the average size of the well-dispersed Au nanoparticles was 3.0 ± 1.0 nm. An EXAFS/XANES analysis showed that the Au nanoparticles were completely metallic in nature.

Under similar reaction conditions, the Au catalysts supported on silylated mesoporous titanosilicates showed greatly enhanced catalytic activity for propene epoxidation (Figure 2, Table 1, catalysts 2–6). The propene conversion and PO selectivity increased conspicuously after silylation of the Au/titanosilicate catalysts. The silylated catalysts with 3 and 6% Ti (catalysts 3 and 5), showed higher propene conversion than the silylated catalyst with 2% Ti (catalyst 2). Further enhancement of epoxidation activity was observed over a silylated catalyst (3 mol% Ti) impregnated with 1 wt% $Ba(NO_3)_2$, which had the highest propylene conversion of 9.8% and about 90% PO selectivity. This catalyst was much more active than Au/Ti-MCM-48 catalyst (Table 1). Enhanced propene conversion and PO selectivity can be attributed to the larger pore size and 3D mesoporosity of the support, which allow easy diffusion of reactants and products, while higher hydrophobicity due to silylation favors ready desorption of PO. It was also possible for the first time to regenerate the catalyst (catalyst 4) and regain about 90–95% of initial activity by treatment in 10 vol% $H_2$ and $O_2$ diluted in argon (for about 1–2 h) at 250 °C. This is very important for making the process commercially viable.

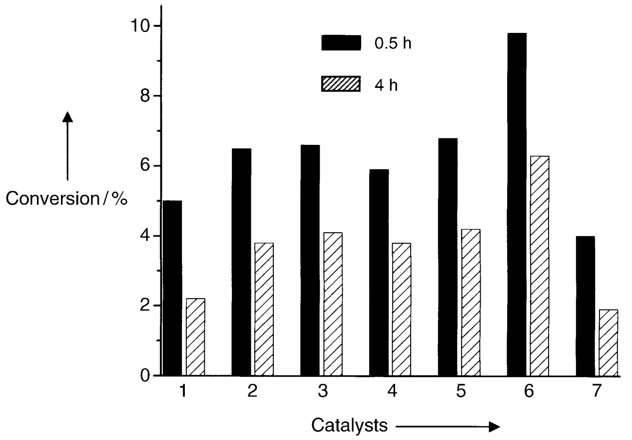

**Figure 2.** Propylene epoxidation over gold nanocatalysts deposited on 3D mesoporous titanosilicate: 1) 2 mol% Ti; 2) silylated catalyst 1; 3) silylated catalyst, 3 mol% Ti; 4) regenerated catalyst 3; 5) silylated catalyst, 6 mol% Ti; 6) $Ba(NO_3)_2$-promoted silylated catalyst 3. (7) Au/Ti-MCM-48.

Propene conversions decreased with on-stream time in all cases, but a relatively lower decrease was observed for silylated catalysts. This is attributable to the easy desorption of PO from the support surface and to passivation of surface acid sites, which prevents deactivation of the catalyst surface by oligomerized species formed from adsorbed PO at these sites.[7] Thus, silylation of Au catalysts supported on disordered titanosilicates has been found to have a very positive

***Table 1:*** Propylene epoxidation over gold nanoparticles deposited on mesoporous titanosilicates and reference materials.

| Catalyst | Ti content (treatment) | TOS [h][a] | Conversion [%] |  | PO selectivity [%] | $H_2$ efficiency [%][b] |
|---|---|---|---|---|---|---|
|  |  |  | $C_3H_6$ | $H_2$ |  |  |
| 1 | 2% | 0.5 | 5.0 | 14.1 | 91.1 | 33.3 |
|  |  | 4 | 2.2 | 7.7 | 95.5 | 41.0 |
| 2 | 2% | 0.5 | 6.5 | 15.7 | 93.3 | 35.3 |
|  | (silylated) | 4 | 3.8 | 9.7 | 96.4 | 34.0 |
| 3 | 3% | 0.5 | 6.6 | 15.8 | 94.9 | 35.4 |
|  | (silylated) | 4.0 | 4.1 | 10.2 | 95.8 | 31.8 |
| 4[c] | 3% | 0.5 | 5.9 | 15.2 | 94.1 | 29.4 |
|  | (silylated) | 4.0 | 3.8 | 10.8 | 94.3 | 27.3 |
| 5 | 6% | 0.5 | 6.8 | 17.5 | 90.1 | 23.6 |
|  | (silylated) | 4.0 | 4.2 | 11.3 | 92.8 | 27.2 |
| 6[d] | 3% | 0.5 | 9.8 | 22.3 | 90.3 | 27.1 |
|  | (silylated) | 4.0 | 6.3 | 16.7 | 92.3 | 34.6 |
| Au/Ti-MCM-48 | 2% | 0.5 | 4.1 | 35.2 | 91.2 | 8.9 |
|  |  | 4 | 1.9 | 33.4 | 92.8 | 4.1 |
| Au/Ti-MCM-48s | 2% | 0.5 | 2.7 | 21.3 | 94.2 | 10.1 |
|  | (silylated) | 4 | 2.3 | 18.8 | 95.5 | 9.6 |

[a] TOS = time on stream. [b] Based on a stoichiometric reaction to produce PO and water. [c] Catalyst 3, regenerated with Ar-diluted $H_2 + O_2$ for 1 h. [d] $Ba(NO_3)_2$-promoted catalyst.

influence on PO yield, in contrast to silylated Au/Ti-MCM-48 catalysts (Table 1). Furthermore, the addition of $Ba(NO_3)_2$ (as a promoter) to the Au/titanosilicate catalyst enhances propylene conversion, probably by promoting the formation of hydroperoxide-like species from $H_2$ and $O_2$, as well as by lowering the acidity of the catalyst. These titanosilicate-based catalysts also showed the best hydrogen efficiency. For example, the $H_2$ consumption was nearly 2–5 times lower than those observed for ordered MCM-type supports (Table 1), and this can be directly correlated to efficient utilization of hydroperoxide-like species generated in situ for epoxidation[3] due to better synergism between Au and Ti sites. The PO concentration in the exit gas for the Ti-MCM-48 based catalyst was about 0.1 vol%, while for catalyst 6 it contained about 1 vol% PO. The activity of the catalyst in terms of space–time yield is 130–150 $\mathrm{g\,L^{-1}\,h^{-1}}$, which is in the desired range to make this process commercially viable. $CO_2$ was the major byproduct of the reaction, and traces of ethanal, propanal, and acetone were also observed.

In summary, we have demonstrated that highly dispersed gold nanoparticles supported on 3D mesoporous, silylated titanosilicates with large (> 7 nm) pores in the presence of $Ba(NO_3)_2$ as a promoter are very efficient catalysts for the epoxidation of propene to PO with molecular $O_2$ and $H_2$. Further work on catalyst preparation, silylation optimization, metal salt promoters, and optimization of the balance between synergetic Au and Ti sites is underway and will result in the preparation of a commercially viable catalyst for propene epoxidation. Furthermore, these 3D mesoporous titanosilicates with a high titanium content (up to 8 mol%) can be expected to be highly active in other oxidation and epoxidation reactions.

## *Experimental Section*

A modified sol–gel method was used to prepare mesoporous titanosilicates.[12] In a typical synthesis, titanium tetra-*n*-butoxide (2.1 g, for 6 mol% Ti) was added dropwise to tetraethyl orthosilicate (20.8 g) while stirring. Then triethanolamine (29.8 g) was added dropwise to the stirred mixture followed by the dropwise addition of deionized water (19.8 g). After stirring the solution for 1–2 h, tetraethylammonium hydroxide (14.7 g) was added dropwise. The final homogeneous mixture was aged at room temperature for 24 h, dried overnight at 100 °C, and then calcined at 700 °C for 10 h in air.

In a typical preparation of titanosilicate-supported Au catalysts by the DP method, an aqueous solution (100 mL) of $HAuCl_4 \cdot 4H_2O$ (2 mmol) was heated to 70 °C, and the pH value was adjusted to 7.0 by adding aqueous NaOH solution. The support (1.0 g) was suspended in the solution, and the pH value was readjusted to 7.0. The suspension was stirred for 1 h, after which the solid was collected by filtration, dried at 100 °C for 12 h, and then calcined at 300 °C for 8 h. The catalyst was placed in a vertical fixed-bed U-shaped quartz reactor (internal diameter = 10 mm) and pretreated in a flow of 10 vol% $H_2$ in Ar and 10 vol% $O_2$ in Ar for 30 min each at 250 °C. The catalysts were trimethylsilylated at 150 °C by passing methoxytrimethylsilane vapor (maintained at 25 °C) in an Ar stream over the catalyst bed for 15–30 min, followed by flushing with Ar at 200 °C (5 h) prior to catalytic measurements. Catalytic epoxidation was carried out at 160 °C with a feed containing 10 vol% each of $C_3H_6$, $H_2$, and $O_2$ in argon (space velocity 4000 $\mathrm{cm^3\,h^{-1}\,g^{-1}}$ cat.). PO selectivity was calculated as: (moles of PO formed/moles of propene converted) × 100.

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