

# A Transient Kinetic Analysis of the Epoxidation of Propene over Gold-Titania Catalysts

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## Introduction

Propene oxide is an important chemical intermediate, produced at about 6 million tons per year (2006) with demand still growing by 5 % annually<sup>1</sup>. One of the new developments for the production of propene oxide are the gold titania based epoxidation catalysts<sup>1-4</sup>. Gold-titania catalysts can selectively epoxidize propene at mild conditions using molecular oxygen in the presence of hydrogen as sacrificial reductant. Because of the use of hydrogen, this reaction is best called a hydro-oxidation rather than an oxidation reaction. Gold-titania based catalyst systems have a number of disadvantages which need to be improved: the conversion levels remain low, often the catalyst stability is insufficient, and the hydrogen efficiency is low<sup>1,5,6</sup>.

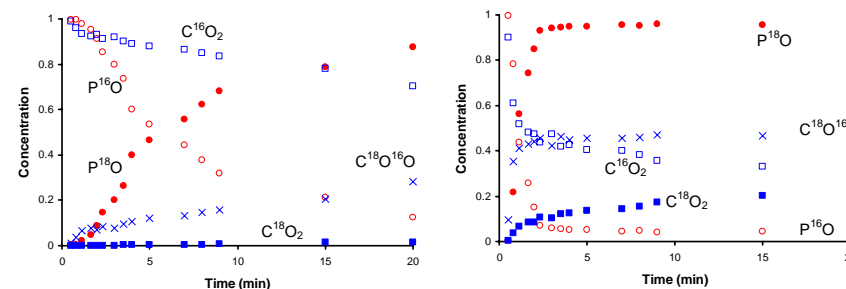
For the hydro-oxidation of propene, it is commonly known that the support plays a crucial role in the reaction. In most studies, it is assumed that the titanium containing support only acts as reaction site for the epoxidation of propene by a peroxo species produced on gold nanoparticles. In previous work<sup>4,7</sup>, we showed that propene could also produce oxygenated surface species on titania without co-feeding oxygen. In this study, we present evidence from transient kinetic experiments that surface oxygen does indeed end up in reaction products.

## Materials and Methods

Gold catalysts were prepared using a deposition-precipitation method on different titania, silica, and silica-titania supports. All catalysts had gold loadings of about 1 wt% and gold particles of 2-6 nm. The catalysts were tested in a flow reactor for their activity in the propene epoxidation and water formation. SSITKA (Steady State Transient Kinetic Analysis) experiments were performed to investigate the origin of oxygen in the reaction products. While the reaction was operated under steady state conditions, an instantaneous switch was made in the feed composition, in which <sup>16</sup>O<sub>2</sub> was replaced by <sup>18</sup>O<sub>2</sub>. By observing the product composition with respect to the type of oxygen in the products and the rate at which this the isotopic switch occurred in the products, mechanistic information on the reaction is obtained. Both on-line mass spectrometry (MS) and GC-MS were used.

## Results and Discussion

In Figures 1 and 2 the isotopic transients are shown for propene oxide and carbon dioxide are shown for a 1 wt% Au/TiO<sub>2</sub> catalyst and a 1 wt% Au/Ti-SBA-15 catalyst respectively. It can be seen that the isotopic transient for propene oxide is considerably faster for the Ti-SBA-15 supported catalyst than it is for the TiO<sub>2</sub> supported catalyst. A first explanation is that support oxygen would be involved in the reaction. Since only the Ti in Ti-SBA-15 (1.5 wt% Ti) is reducible, the oxygen donating capacity of this material is much lower



**Figure 1.** SSITKA isotopic transient for propene hydro-epoxidation over a 1 wt% Au/TiO<sub>2</sub> catalyst. <sup>16</sup>O<sub>2</sub>-<sup>18</sup>O<sub>2</sub> switch at steady state (323 K, GHSV=9000 h<sup>-1</sup>)

**Figure 2.** SSITKA isotopic transient for propene hydro-epoxidation over a 1 wt% Au/Ti-SBA-15 catalyst. <sup>16</sup>O<sub>2</sub>-<sup>18</sup>O<sub>2</sub> switch at steady state (373 K, GHSV=9000 h<sup>-1</sup>)

than that of bulk TiO<sub>2</sub>. An alternative explanation would be that the adsorption of propene oxide is much stronger on TiO<sub>2</sub> than on Ti-SBA-15. Additional experiments to be presented at the conference will be able to distinguish between these two possibilities.

The transient for CO<sub>2</sub> is even slower than that of propene oxide. Furthermore, the formation of first single labeled C<sup>18</sup>O<sup>16</sup>O before C<sup>18</sup>O<sub>2</sub> is clear evidence for CO<sub>2</sub> being formed in a two-step oxidation process, in which again support oxygen seems to be playing an important role. The two-step formation of CO<sub>2</sub> is in agreement with observations we made previously using in-situ infrared experiments<sup>4,7</sup>.

It can be concluded that transient kinetic experiments are a very valuable tool for investigating the complex mechanistic of the hydro-epoxidation of propene. The results of this study will be presented and combined with other techniques and a reaction mechanism will be presented.

## Significance

Gold-titania catalysts are very promising for a future propene epoxidation process, but they still need to be improved with respect to activity and stability. The insight this study provides in the mechanism of this system will be of great help in the development of better catalysts.

## References

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