

DIRECT EPOXIDATION OF PROPENE OVER GOLD-TITANIA CATALYSTS: A TRANSIENT STUDY OF THE REACTION MECHANISM

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Summary

Gold-titania based catalysts for the direct epoxidation of propene provide a clean and simple route for future propene oxide producing processes. These catalysts, producing propene oxide in a single step, have a moderate activity and a very high selectivity towards propene oxide. However, the hydrogen, which is used as a co-reactant, is used less efficient. To be able to improve the hydrogen efficiency as well as the catalyst stability, mechanistic knowledge on the catalyst is essential. A (transient) kinetic study has been performed, aided by in-situ spectroscopic measurements. This study will be presented together with recommendations on how to develop improved catalysts for this system.

Keywords

Reaction Path Analysis, Sustainability.

Introduction

Propene oxide is an important chemical intermediate, produced at about 6 million tons per year (2006) with demand still growing¹. A new development for the production of propene oxide is the gold titania based epoxidation catalyst¹⁻⁴. 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^{1,5}. A recent breakthrough discovery by Ojeda and Iglesia⁶ showed that the reaction can also be performed using oxygen combined with a water instead of hydrogen. The activity of this system is lower, but this disadvantage is easily compensated by the lower costs of the reactants.

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 peroxy species produced on gold nanoparticles. In previous work^{4,7}, we showed that propene could also produce oxygenated surface species on titania without co-feeding oxygen, indicating that support oxygen might play a role in the reaction mechanism. In this study we present transient kinetic experiments⁸ using isotopic labeled oxygen to elucidate the role of surface oxygen in the reaction. Kinetic experiments in a microreactor system,

allowing us to extend the concentration window into the explosive region, provide additional information. The epoxidation of propene using a water-oxygen mixture was included in the kinetic study to determine similarities in the reaction pathways for the hydrogen/oxygen and the oxygen/water epoxidation mechanisms.

Experimental

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 characterized using TEM, in-situ XAFS, and in-situ infrared spectroscopy.

Catalytic experiments were carried out at different feed concentrations in a flow reactor to determine the reaction kinetics in the propene epoxidation and water formation. Using a microreactor for these experiments, allowed us to extend the concentration range for the kinetic experiments inside the explosion regime.

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 ¹⁶O₂ was replaced by ¹⁸O₂. 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 for the analysis of the SSITKA responses.

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Results and Discussion

In Figure 1, as an example, the isotopic transients in a SSITKA experiment are shown for propene oxide, carbon dioxide, and water for a 1 wt% Au/Ti-SBA-15 catalyst. The transients are all significantly slower than the switching time for the gas phase, which is in the order of 3 seconds. This is a strong indication that either product desorption is a rate limiting step, or that support oxygen is playing a role in the reaction mechanism. The isotopic transients for the TiO₂ supported catalysts were even significantly slower (PO transient takes 40 minutes), which indicates the use of support oxygen, since the amount of (reducible) Ti in the supports and thereby the oxygen donating capacity was higher for this catalyst.

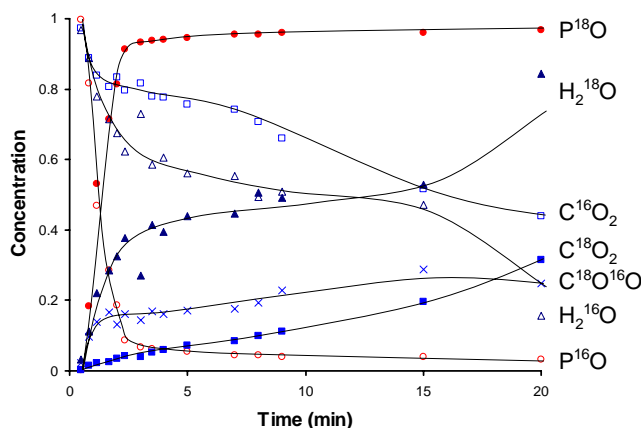


Figure 1. SSITKA transients for switch from $^{16}\text{O}_2$ to $^{18}\text{O}_2$ for propene epoxidation over a 1 wt% Au/Ti-SBA-15 catalyst at 423 K.

By taking the area under the isotopic breakthrough curves from the SSITKA experiments and combining that with the catalytic activity, it is possible to quantify the amount of absorbed oxygen (as oxygen or partially oxidized reactants) and oxygen donated by the support. These values are provided in Table 1.

Table 1. Amounts of ^{16}O containing products produced over Au on TiO₂ and Ti-SBA-15 after switching to $^{18}\text{O}_2$ determined by integration of the isotopic transients.

Support:	TiO ₂	Ti-SBA-15	
Propene oxide-16	26.3	18.3	μmol/g
C ¹⁸ O ¹⁶ O	1.6	2.4	μmol/g
C ¹⁶ O ₂	8	120	μmol/g
H ₂ ¹⁶ O	15400	5130	μmol/g

For the TiO₂ support, the amount of 16-O in the products is significantly larger than the number of Ti-surface sites (830 μmol/g), thereby ruling out physical adsorption as a possible explanation, and of the same order of magnitude as the total amount of oxygen in the support (25000 μmol/g), which is evidence for either an involvement of the support oxygen in the formation of the products, or an

oxygen exchange with the support afterwards. Gold is a requirement for these catalysts to have any catalytic activity and we also observed using previous in-situ infrared experiments^{4,7} that partially oxidized surface species were formed near gold. The amount of available Ti sites near gold, however, is smaller (1 μmol/g) than the amount of unlabeled propene oxide and CO₂ released after the isotopic transient.

For the Ti-SBA-15 supported catalyst the surface area is much larger: 490 m²/g, corresponding to approximately 6240 μmol/g surface Si and 420 μmol/g surface Ti. Physical adsorption would therefore be a possible explanation. Additional experiments will be performed to make a distinction between the use of adsorbed species containing oxygen, the use of support oxygen in the reaction, and the exchange between oxygen in the reaction products and support oxygen.

Kinetic modeling of the catalytic experiments indicates that product desorption is a rate limiting step in the reaction mechanism at the low concentration regime (<10 vol% for each reactant) typically used for this reaction. Work is currently in progress to determine if is still valid when the reaction is carried out with higher reactant concentrations, considering the significantly higher yields that were reported by Oyama *et al.*⁹ when the reaction was carried out in a membrane reactor in the explosive regime.

Conclusions

Transient kinetic experiments are a very valuable tool for investigating the complex mechanism of the hydro-epoxidation of propene. Support oxygen is involved in the reaction mechanism. The results of the transient experiments will be presented and combined with kinetic experiment to determine the reaction mechanism.

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