

The Kinetics of the Propene Epoxidation and Water Formation over Gold-Titania Catalysts

T. Alexander Nijhuis^{1*} and Bert M. Weckhuysen²

¹Eindhoven University, Chemical Reactor Engineering, P.O. Box 513, Helix - STW 1.26
5600 MB Eindhoven (The Netherlands)

²Utrecht University, Inorganic Chemistry and Catalysis, Sorbonnelaan 16,
3584 CA Utrecht (The Netherlands)

*t.a.nijhuis@tue.nl

Introduction

Propene oxide is a very important chemical intermediate, produced at about 6 million tons per year (2006) with demand still growing by 5 % annually¹. One of the important new developments for the production of propene oxide are the gold titania based epoxidation catalysts¹⁻⁴. Gold-titania catalysts can very selectively epoxidize propene at mild conditions using molecular oxygen in the presence of hydrogen as sacrificial reductant. Because of the use of sacrificial 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^{1,5,6}. The hydrogen efficiency (defined as the amount of propene oxide produced divided by the hydrogen consumed) is dominated by the water produced by the direct hydrogen oxidation. The low hydrogen efficiency is the most important problem that needs to be solved before this catalyst system can be applied commercially. This paper presents a kinetic study into the hydrogen oxidation. Both the behavior of gold on titania, the 'standard' catalysts of choice for the propene hydro-epoxidation, and the behavior of gold on silica are investigated. Gold on silica does not have any significant propene epoxidation activity and is studied to investigate the possible role of the support and as a way to de-couple the epoxidation from the water formation. For the hydro-oxidation of propene, it is commonly known that the support plays a crucial role in the reaction^{4,7}.

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. The catalytic activity was typically tested for a period of 5-10 days, during which the conditions were varied and aspects like catalyst activation and deactivation were investigated. The catalytic performance combined with results from different catalyst characterizations was used to derive kinetic models.

Results and Discussion

Figure 1 shows the propene epoxidation and water formation over a gold/titania catalyst. It can be seen that without propene present, the catalytic activity for the hydrogen oxidation is one order of magnitude higher. Furthermore, without propene there is no catalyst deactivation. For this system, the removal of propene does not result in a recovery for the catalytic activity. The hydrogen oxidation over a gold on silica catalyst is surprisingly also affected by propene (Figure 2), even though this catalyst does not convert any measurable

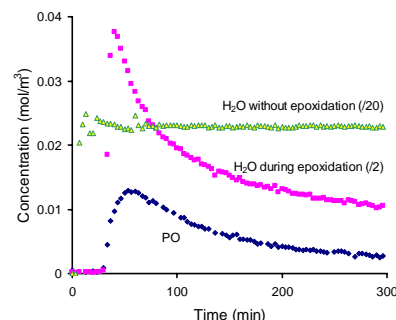


Figure 1. Propene oxide and water formation over a 1 wt% Au/TiO₂ catalyst. Activity during epoxidation and hydrogen oxidation without propene. (325 K, GHSV=9000 h⁻¹)

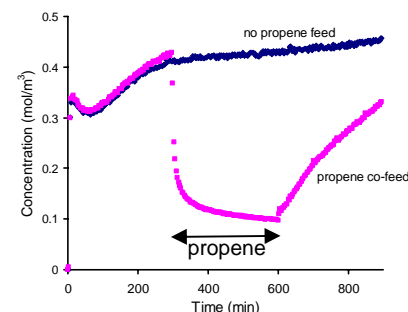


Figure 2. Water production during hydrogen oxidation over 1 wt% Au/SiO₂ catalyst. In one cycle propene is co-fed to the reaction mixture for 5 hours. (353 K, GHSV=9000 h⁻¹)

quantity of propene. In this case, however, the activity does recover, although slowly, once propene is removed. For water a similarly strong effect on the catalytic activity was observed.

It can be concluded that there is a strong correlation between the epoxidation and the water formation. During the epoxidation, the water formation is strongly suppressed, which is partly caused by adsorption of propene oxide on the catalyst, and partly by propene adsorption on the gold particles. Water slows down both the water formation and the epoxidation reaction, the self-inhibiting effect on the water formation is strongest, making co-feeding water a convenient way to improve the hydrogen efficiency. As an added advantage, co-feeding water reduced the catalyst deactivation process. A mechanistic study into epoxidation and water formation will be presented, together with approaches how to reduce the water formation and thereby improve the attractiveness of this gold-titania catalyst system.

Significance

Gold-titania catalysts are very promising for a future propene epoxidation process. One of the most important challenges for these catalysts to be solved is the low hydrogen efficiency. This study presents mechanistic information on the water formation and ways how to improve the hydrogen efficiency by reducing the water production.

References

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