One-Pot Synthesis of Epoxides from Hydrogen, Oxygen and Alkenes -A way to process intensification?

Christoph Schmidt[1], Matias Alvear[1], Francesco Sandri[1], Seo Mandon[2], Alice Vidrequin[3], Jeremy Favier[3], Tiina Laitinen[4], Satu Ojala[4], Kari Eränen[1], Tapio Salmi[1]*

1 Laboratory of Industrial Chemistry and Reaction Engineering (TKR), Åbo Akademi University, 20500 Turku/Åbo, Finland;

2 École des métiers de l'environnement, UniLaSalle Rennes, 35170 Bruz, France;

3 Faculté des Sciences Fondamentales et Appliquées, Université de Poitiers, 86073 Poitiers, France;

4 Environmental and Chemical Engineering, University of Oulu, 90014 Oulu, Finland

**Corresponding author: tapio.salmi@abo.fi*

Highlights

- Combined DSHP and HPPO in liquid phase at mild conditions successfully demonstrated.
- Dependency of AuPd nanoparticle deposition behavior on anatase in commercial TS-1.
- Propylene oxide selectivity enhancement by gold-rich alloy and larger AuPd nanoparticles.
- Integrated process more efficient than separated reactions.

1. Introduction

Propylene oxide is a key intermediate in the chemical industry, for instance for the production of polyurethane foams [1]. Several industrial production routes has been established, which are considered as environmentally unfriendly as they involve molecular chlorine or toxic organic peroxide-species [2]. A greener alternative is the hydrogen peroxide to propylene oxide (HPPO) process, which utilize biodegradable hydrogen peroxide as oxidant and propene, forming propylene oxide and water as co-product [3]. Hydrogen peroxide is currently produced by the antraquinone process, which suffer from several disadvantages, including low process efficiency, generation of large amounts of waste and catalyst deactivation [4]. The direct synthesis of hydrogen peroxide (DSHP) from hydrogen and oxygen offers a cleaner route for the production of hydrogen peroxide (H_2O_2), with water as the only by-product. Unlike the anthraquinone process, DSHP can be operated on a smaller scale and integrated directly with existing processes, for instance the epoxidation of olefins, enabling decentralized and more sustainable production [5].

2. Methods

AuPd/TS-1 catalysts were synthesized by a co-deposition-precipitation method using $PdCl_2$, HCl, $HAuCl_4 \cdot 3\,H_2O$, urea and TS-1. The slurry was vigorously stirred and heated to 80 °C. After 4–18 h of heating, the slurry was cooled under continuous stirring, filtered, and, depending on the catalyst preparation protocol, washed, dried and calcined. The catalysts were characterized using several techniques, including STEM-EDS and TEM-SAED.

Catalytic experiments were performed in a setup with an integrated co-current trickle bed reactor with temperature and pressure control. Typical experiments were conducted at 8 bar, 10 °C, a gas flow rate of 40 $ml \cdot min^{-1}$ (at atm), and a liquid flow rate of 1 $ml \cdot min^{-1}$. The gas feed composition consisted of 0.07 $mmol \cdot min^{-1}$ H_2, 0.07 $mmol \cdot min^{-1}$ O_2, 0.14 $mmol \cdot min^{-1}$ propene and 1.46 $mmol \cdot min^{-1}$ CO_2, while methanol was used as the liquid phase. For the catalyst bed, 1 g of catalyst was diluted with 20 g of sand. Gas and liquid samples were continuously collected and analyzed by GC, UV-Vis spectrometry for H_2O_2 quantification and Karl-Fischer titration. Conversion, selectivity and productivity were subsequently determined.

3. Results and discussion

Active AuPd/TS-1 catalysts of the combined reaction DSHP and propene epoxidation were successfully synthesized and characterized. Anatase impurities were found in the commercial TS-1 materials. The quantity of anatase had a significant influence on both metal nanoparticles size and metal distribution, as anatase was the preferred deposition site. In contrast, anatase-free TS-1 resulted in a homogenous metal deposition across the support. The duration of the urea-assisted synthesis and the following washing process strongly affected catalysts activity. Longer synthesis time and water washing only yielded the highest catalyst activity in the combined reaction. The alloy composition of metal nanoparticles of the catalyst was found to be crucial for the efficiency of the reaction system, suppressing undesired propene hydrogenation and excessive water formation. The one-pot reaction was further investigated towards product distribution governed by reaction temperature, liquid flow rate and reactant composition. The variation of these parameters revealed clear trends, providing insights into the behavior of the sequential reaction system.

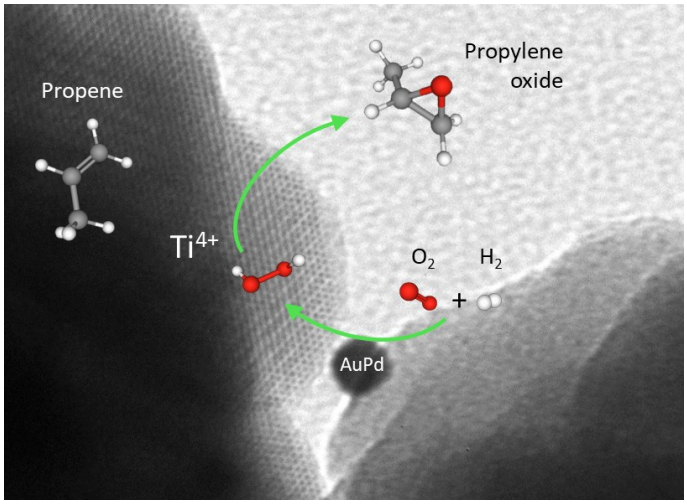

Figure 1. Scheme of the one-pot reaction sequence on the active sites of the AuPd/TS-1 catalyst [6].

4. Conclusions

The one-pot synthesis of propylene oxide from hydrogen, oxygen and propene was successfully demonstrated. Bifunctional AuPd/TS-1 catalysts were synthesized and characterized, revealing that anatase impurities in the TS-1 material significantly influenced the metal deposition. Optimization of both catalyst synthesis and reaction parameter enhanced the overall efficiency of the reaction system and identified key parameter governing catalytic performance.

References

[1] T. Miyazaki, S. Ozturk, I. Onal, S. Senkan, Catal. Today. 81 (2003) 473-484
[2] T.A. Nijhuis, M. Makkee, J.A. Moulijn, B.M. Weckhuysen, Ind. Eng. Chem. Res, 45 (2006) 3447-3459
[3] P. Bassler, M. Weidenbach, H. Goebbel, Chem. Eng. Trans. 21 (2010) 571-576
[4] J.M. Campos-Martin, G. Blanco-Brieva, J.L.G. Fierro, Angew. Chemie Int. Ed. 45 (2006) 6962-6984
[5] P. Biasi, P. Canu, F. Pinna, T. Salmi, Chem. Eng. Trans. 24 (2011) 49-54
[6] C. Schmidt, M. Alvear, F. Sandri, S. Mandon, S. Ojala, T. Laitinen, M. Lastusaari, I. Angervo, T. Salmi, J. Cat. 454 (2026) 116637

Keywords
Propylene oxide; Hydrogen peroxide; Gold-palladium catalyst; One-pot synthesis.