

Novel low pressure and temperature production technology of propylene oxide from oxygen, hydrogen and propene in a trickle-bed reactor

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Highlights

- First successful one-pot epoxidation of propene under low temperature and pressure with hydrogen and oxygen
- Successful development of catalyst synthesis for AuPd on titanium silicalite TS-1
- Catalysts have been active for the one-pot epoxidation and were improved

1. Introduction

H₂O₂ is a strong oxidant that is widely used as a bleaching agent in the paper and textile industries. Furthermore, H₂O₂ is also used as a reactant to produce epoxides and other compounds in the chemical industry. The industrial anthraquinone process covers the demand of H₂O₂ until now, despite its drawbacks concerning side reactions, accumulation of impurities and catalyst deactivation during the hydrogenation step. An alternative reaction route is the direct synthesis of hydrogen peroxide (DSHP) from the elements, which displays an environmental-friendly route considering the atom efficiency as well as the avoidance of toxic waste. Moreover, a big advantage of DSHP is the straightforward process setup and separation of the product from the solvent, which is a critical issue in the anthraquinone process. This feature enables an on-site production of hydrogen peroxide, being integrated or combined with processes such as alkene epoxidation. DSHP would overcome the non-environmental-friendly anthraquinone process and avoid transportation costs. In 1998, Hayashi et. al. discovered that Au/TS-1 is able to perform propene epoxidation in the presence of hydrogen and oxygen in gas phase^[1]. Since this discovery, there has been more approaches for the epoxidation of propene at high temperature in gas phase or in supercritical CO₂ to produce propylene oxide with oxygen and hydrogen via in-situ generated hydrogen peroxide^{[2][3]}, which all require high-energy input. This is however unattractive for industrial application. In this work, a novel concept is presented, where the reaction is conducted under mild conditions in a trickle bed reactor. The performance of the system was improved by the development of new AuPd-based catalysts.

2. Methods

AuPd/TS-1 catalysts were prepared via urea-deposition, where gold and palladium are co-precipitated. The duration of the synthesis was 15 h. After, the catalysts were washed with NH₄OH and water, and filtered. The as-synthesized catalysts were dried and calcined with different heating rates between 1.5 – 10 K/min at a final calcination temperature of 300 °C for 3 h. The catalysts were characterized with nitrogen physisorption, ammonia temperature-programmed desorption (NH₃-TPD), diffuse reflectance UV-vis spectroscopy (DRS), scanning electron microscopy (SEM) and transmission electron microscopy (TEM), X-ray diffraction (XRD). The metal content was determined with ICP-MS.

Performance experiments were carried out in a tailored laboratory-scale trickle bed reactor and the components were analyzed with micro-GC, GC, UV-vis spectroscopy, and Karl-Fischer titration. Typical reaction conditions were 10 °C and 8 bar. The reactor was fed with 0.07 mmol/min hydrogen and oxygen, 0.14 mmol/min propene and 1.46 mmol/min carbon dioxide. Methanol was used as the solvent with a flow rate of 1 ml/min.

3. Results and discussion

Two batches of catalysts were prepared where an uneven deposition pattern onto different morphologies of TS-1 were found. The majority of the AuPd nanoparticles were found onto squared TS-1 particles while spherical TS-1 particles were less occupied. Moreover, the nanoparticle size distribution depends on the species of particle where a narrower smaller range of 3 – 7 nm was found for AuPd on squared particles while on the spherical TS-1 the nanoparticles were 3 – 16 nm. In the catalytic tests, a steady increase of hydrogen peroxide production led to a constant increase of the propylene oxide selectivity. The selectivity was also dependent on the palladium loading: with less palladium, a tremendous increase of the selectivity was recognized because of suppressing the competing hydrogenation of propene. In the first batch of catalysts, the selectivity of propylene oxide was 29 % and a maximum propylene production of 0.012 mmol/min/g_{cat} was achieved while in the second batch, the selectivity increased up to 66 % with a decreased propylene oxide productivity of 0.004 mmol/min/g_{cat}. For a selected catalyst, a reusability test was conducted and it showed an excellent catalyst stability where even a slight activation was found. In addition, the separate reaction of DSHP and HPPO was conducted for a deeper understanding of the reaction system. The results will be presented in detail at the conference.

4. Conclusions

In this work, a novel approach was presented to produce propylene oxide from hydrogen, oxygen, and propene in a trickle bed reactor. A suitable catalyst synthesis method was developed for the AuPd/TS-1 catalysts which have been active for the one-pot synthesis of propylene oxide. Furthermore, the influence of the chemical composition of the catalysts on the selectivity was demonstrated. The excellent catalyst stability was proofed by reusability tests and total time-on-stream (TOS) experiments. The present results demonstrates an alternative and attractive synthesis route for the HPPO process to obtain high-valuable propylene oxide. The potential for an industrial application was demonstrated by the improved selectivity and long-term stability for the continuous process.

References

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Keywords

propylene oxide, epoxidation, trickle bed reactor, catalyst