Propene epoxidation over titanium silicate catalyst a new understanding

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Highlights

- Propene epoxidation was studied in laboratory scale reactor and with spectroscopic techniques.
- The experimental and modeling campaign comparison of sites structures proposed in the literature suggests new insights.
- The utilization of modulation spectroscopy allows the observation of the effects of additives in the reaction system.

1. Introduction

The discovery of titanium silicates around 40 years ago enabled the development of a more sustainable method for producing epoxides from alkenes and hydrogen peroxide. The present study aims to enhance the understanding of the epoxidation reaction on titanium silicates. Observing differences at the reactor level provides clarity on the significance of molecular structure concerning product distribution and catalyst stability. A modulation excitation study revealed variations in titanium site interactions, contingent on the catalyst structure, suggesting that the additives influence the behavior of the active site.

2. Results and discussion

An extensive series of transient and stationary epoxidation experiments involving several alkenes was conducted in a laboratory-scale trickle bed reactor loaded with TS-1. Gas chromatography (GC) was utilized for reactant and product analysis. The results indicate changes in transient behavior with increasing carbon chain length (ethylene, propylene, and 1-butene). New side reactions were observed due to the ring opening of isobutene epoxide. The molecular structure of the alkene was found to be a crucial element in determining epoxide selectivity and yield.

Differences in behavior observed in the reactor experiments, as well as findings in the literature, highlighted the need to analyze reactant-catalyst interactions in epoxidation. In this study, we employed in-situ spectroscopy. Our approach involved applying modulation excitation Fourier-transform infrared (FTIR) spectroscopy to observe changes in titanium site vibrations. Water, methanol, acetonitrile, hydrogen peroxide, and propylene were modulated to observe differences in the behavior of the TS-1 active site.

The effect of modulation on the titanium site activation was analyzed. The results of the hydrogen peroxide modulation experiments are presented in Figure 1. Modulation of hydrogen peroxide over TS-1 catalyst resulted in the observation of two bands related, one from the H_2O_2 in the bulk of the liquid and the other from the adsorbed over the surface. This study highlights significant differences in the TOF by the presence of low concentrations of additives in the liquid phase. among the various titanium silicate systems investigated.

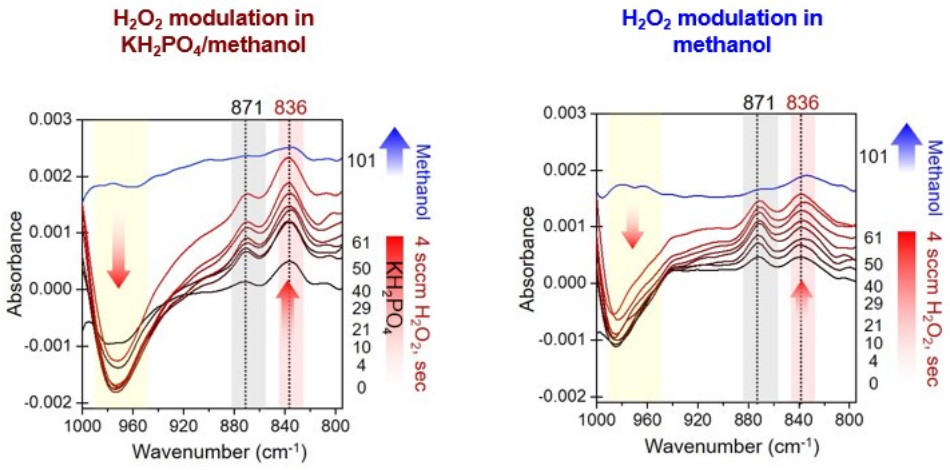

Figure 1. Additive effect in the modulation of hydrogen peroxide, MES experiments. 0.1wt%H_2O/MeOH vs MeOH at 30 ºC and 1 bar.

4. Conclusions

The study of the epoxidation reaction using transient techniques has provided valuable insights into the active site. Analyzing the titanium sites proposed in the literature has revealed significant similarities in the computational studies, offering new ideas into the epoxidation mechanism. Additionally, the additive studies have identified general differences in the epoxidation process that were not reported previously.

References

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Keywords

Titaniumsilicate, epoxidation, propene and hydrogen peroxide