An In-Situ FTIR Investigation of the Oxidation of Allyl Alcohol by Titanium Silicalite-1 (TS-1)

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Abstract: The partial oxidation of allyl alcohol over titanium silicalite-1 (TS-1) using hydrogen peroxide is examined using operando FTIR spectroscopy. It was found that re-heating the catalyst after the application of hydrogen peroxide may produce a species on the catalyst surface which oxidizes the allyl alcohol vinyl functionality to carbonyl.

Keywords: TS-1, FTIR, selective oxidation.

1. Introduction

The current market oversupply of glycerol due largely to the increased global production of biodiesel has necessitated the development of mitigation strategies. One means of achieving this is through the production of desirable, value-added compounds from waste glycerol. Glycidol (2,3-epoxy-1-propanol) is one such compound, which may be prepared through the epoxidation of allyl alcohol (1-propen-3-ol) obtained by heating glycerol over an alumina-supported iron oxide catalyst[1-2].

Titanium silicalite (TS-1) is a highly stable, fully heterogeneous catalyst suitable for a number of reactions, in particular the exceptionally selective partial oxidation of functionalized olefins to the corresponding epoxide using hydrogen peroxide as an oxidizer[3].

In order to gain insight into the interaction between TS-1, hydrogen peroxide and further, the oxidizing complex with an organic substrate, operando FTIR was employed.

2. Experimental

Titanium silicalite-1 was prepared according to the conventional method published by Taramasso et al.[4] Operando FTIR experiments were performed by mounting a self-supported TS-1 wafer weighing between 5 and 10 mg in a custom-built FTIR cell fitted with KBr or ZnSe windows. The wafer was then activated at 723 K for one hour at 10^{-6} mbar to remove extraneous moisture and organic material. The cell was then opened and the wafer dosed with one drop of 30 wt% aqueous hydrogen peroxide before re-evacuating the cell at 10^{-6} mbar for 12 hours.

Allyl alcohol and other substrates were then dosed onto the wafer through the vacuum manifold for one minute. Spectra were then taken over one hour at 20 second intervals.

3. Results and discussion

The IR spectrum of the TS-1 samples show a characteristic band at 960 cm^{-1} attributed to the perturbation of the silicalite framework vibrations due to the isomorphic substitution of titanium. This vibration is not present in the spectra of the silicalite samples.

Upon addition of hydrogen peroxide to the catalyst wafer, a characteristic color change from white to yellow is observed. This is attributed to ligand-metal charge transfer (LMCT) from the peroxo ligand to the Ti center, and absorbs at a wavelength of around 26,000 cm^{-1} [5], producing the yellow coloration and indicating the formation of the active oxidizing species.

The addition of hydrogen peroxide produces a vibration at 874 cm^{-1} (Figure 1*a*). Bands at 3447 and 1675 cm^{-1} associated with υ(OH) stretching and δ(OH) bending modes of water and/or peroxide, respectively are also produced. These OH vibrations are persistent under vacuum conditions at room temperature, however heating the sample to 723 K completely removes these bands, indicating the complete dehydration/dehydroxylation of the sample. The 874 cm^{-1} band remains largely persistent, even after heating, however subsequent adsorption of allyl alcohol sees it reduce substantially in intensity (Figure 1*b*).

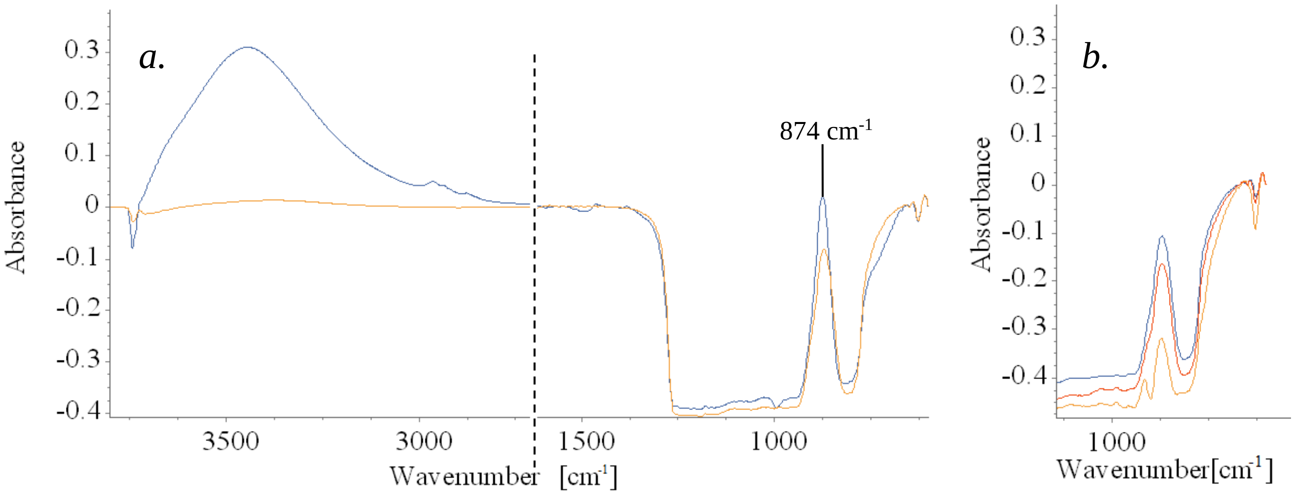

Figure 1: (*a*) Hydrogen peroxide-doped TS-1 before (blue) and after heating (orange). (*b*) Effect of allyl alcohol adsorption on 874 cm^{-1} vibration

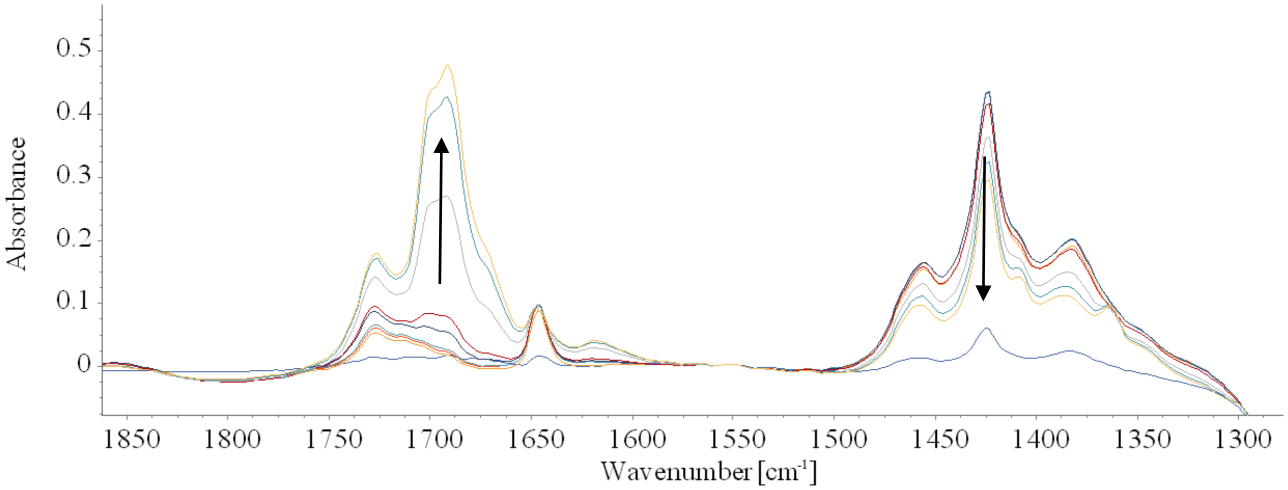

Figure 2: Vinyl (1424 cm^{-1}) and carbonyl (1691 cm^{-1}) vibrations over course of experiment. Arrows indicate change in intensity.

Also observed with the adsorption of allyl alcohol (Figure 2) is the proportional reduction in intensity of the allyl vinyl vibration (1424 cm^{-1}) with the rise of a carbonyl vibration (1691 cm^{-1}). No epoxide vibration was observed in any of the experiments.

4. Conclusions

It appears that under these conditions, a thermally stable oxidizing species giving rise to the 874 cm^{-1} vibration is formed. This species is likely different to the one which engages in the epoxidation reaction, however it is able to partially oxidize the allylic vinyl group to carbonyl.

References

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