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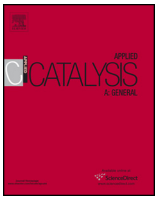

# Influence of impurities on the epoxidation of allyl alcohol to glycidol with hydrogen peroxide over titanium silicate TS-1

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ABSTRACT

The epoxidation of allyl alcohol to glycidol by hydrogen peroxide over titanium silicate TS-1 ZSM-5 has been studied under conditions relevant for an industrial-scale process. In particular, the effects of different solvents, impurities and some side reactions known to occur due to those impurities have been examined. It was found that certain aldehydes (in particular, acrolein) are especially detrimental to glycidol yield. Conversely, some of the impurities added to the reaction mixture were found to promote the conversion of allyl alcohol. Possible mechanisms for this are discussed.

## 1. Introduction

With the predicted global increase in biodiesel production, it is anticipated that a market oversupply of glycerol, the major byproduct (approximately 10 wt%) of biodiesel manufacture, will occur [1,2]. It is thus desirable to produce value-added species from waste glycerol. One commercially attractive product is glycidol (2,3-epoxy-1-propanol), a stabiliser used in the manufacture of vinyl polymers, oil additive and a precursor to novel energetic polymeric compounds. In principle, glycerol may be dehydrated to glycidol and computational chemistry experiments show that the reaction could occur at relatively high temperatures [3,4]. Hydride transfer and substitution mechanisms have been proposed [4] for the conversion of protonated glycerol under acidic conditions, having energy barriers between 21 and 25 kcal $\text{mol}^{-1}$. These reactions may become commercially important in the near future. Glycerol can also be converted to glycidol through allyl alcohol (prop-2-en-1-ol) via either a single step or two step process using alumina-supported iron oxide catalysts [5,6]. The unsaturated alcohol may then be epoxidised to glycidol using organic hydroperoxides (Fig. 1) in an aprotic organic solvent such as benzene over a range of supported transition metal catalysts, most significantly silica-supported titania [7,8]. Other supported metal catalysts, in particular silica-supported molybdena ($MoO_3$), have been shown to effectively catalyse the epoxidation, however that activity has been attributed to rapid leaching of the molybdenum from the catalyst surface to yield a soluble molybdenum catalyst ($MoO_3$-insoluble and $Mo(CO)_6$-soluble, are also catalysts [9]). Other silica-supported metal oxides (e.g. $V_2O_5$, $WO_3$, $TiO_2$) in this system work via a similar mechanism. The silica-supported titania catalyst developed by Shell [10] was found to be truly heterogeneous, as it was both highly active and not subject to metal leaching. All of the silica-supported metal oxide catalysts were found to be severely hindered by the presence of water, due to competition with peroxides for the active catalyst sites. This limited the use of oxidising agents for the reaction to ecologically harmful organic peroxides, particularly *tert*-butyl hydroperoxide. Titanium silicate MFI (TS-1) was first produced in 1983 by Taramasso et al. [11] and was found to be substantially less adversely affected by water [12–14], meaning that hydrogen peroxide (normally supplied in a 30 wt% aqueous solution) could then be used as a more environmentally benign oxidising agent. More recently, other titanium-containing zeolite topologies such as Ti-MWW or Ti-SBA-15 have been prepared in response to the limitation of TS-1 accommodating only smaller substrates such as linear olefins. Ti-MWW has been shown to be superior to TS-1 and Ti-BEA as an epoxidation catalyst under most conditions [15,16], however has gained less traction commercially. This study focuses primarily on catalytic systems in large-scale applications and hence TS-1 was used. Future studies are intended to explore Ti-MWW as an epoxidation catalyst.

Allyl alcohol in particular presents certain obstacles to epoxidation. The hydroxyl group draws electron density away from

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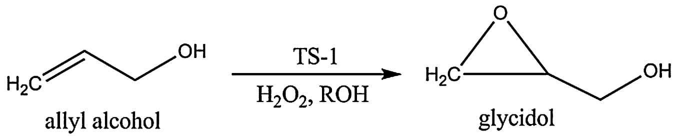

**Fig. 1.** Epoxidation of allyl alcohol to glycidol by hydrogen peroxide under TS-1 catalyst (*R* corresponds to a carbon chain generally of length 1–3).

the carbon double bond, rendering it less susceptible to attack by an electrophilic oxidising agent such as hydrogen peroxide [17]. Furthermore, under certain reaction conditions the epoxide moiety is susceptible to ring-opening reactions followed by nucleophilic attack to yield either glycerol by hydrolysis or diols by solvolysis.

The primary focus of this study is to investigate the influence of the purity of the allyl alcohol reactant mixture, in particular, the effect of varying concentrations of impurities likely to be encountered in the production of allyl alcohol from waste glycerol derived from biodiesel manufacture.

## 2. Experimental

### 2.1. Catalyst synthesis

The TS-1 used in all experiments was prepared as per Taramasso et al. [11], where 37.99 g (0.182 mol) of tetraethylorthosilicate (TEOS, Merck) and 0.61 g (0.003 mol) tetratethylorthotitanate (TEOT, Merck) were mixed at 35 °C. The mixture was then cooled in an ice bath and 39.54 g (0.194 mol) of tetraethylammonium hydroxide (TPAOH) template (40 wt% in water, Merck) was added dropwise using a burette. Following addition of the template, the mixture was heated to 80 °C in order to evaporate ethanol produced by hydrolysis of TEOS. Distilled water was added to return the mixture to its initial volume. The pH was found to be 12.7, close to the published value of 12.2 [11]. The mixture was then transferred to a PTFE-lined stainless steel autoclave fitted with a thermocouple, pressure gauge and pressure relief valve, and heated to 175 °C for two days. The solid product was collected by centrifuging three times for 30 min each at 4000 rpm, washing with distilled water between extractions. The centrifuged product was dried for 5 h at 120 °C, yielding 11.47 g of fine white solid which was heated first in nitrogen at 450 °C for 2 h, left to cool to ambient temperature and subsequently calcined in air at 550 °C for 20 h. The temperature ramp rate for both heat treatments was 2 °C $min^{-1}$. X-ray diffraction using a Phillips X'pert Pro diffractometer with Cu $K_\alpha$ incident radiation ($\lambda$ = 1.5406 Å) was used to characterise the catalyst and compare it to samples synthesised elsewhere [18]. The surface area was determined by nitrogen adsorption and found using Langmuir isotherm to be 563 $m^2\,g^{-1}$.

### 2.2. Epoxidation of allyl alcohol

In a typical experiment, 0.25 g of TS-1, 2.90 g (0.05 mol) of allyl alcohol (Sigma-Aldrich) and 22.5 mL of solvent were added to a 100 mL round bottomed flask fitted with a reflux condenser, thermocouple and septum. The reactants were then heated to the required temperature and 5.67 g of hydrogen peroxide (0.05 mol, 30 wt% aqueous) were added. In particular, the effects of solvent type, reaction temperature and the influence of impurities such as acrolein (propenal) likely to be encountered when conducting the reaction on a large scale were investigated. Molecular properties of the added impurities, in particular atomic charges and dipole moment, were calculated using the B3LYP/6-31G* basis set in density functional calculations in Spartan "10 [19].

A mixture containing allyl alcohol produced in a fixed bed reactor from the conversion of a 30 wt% solution of glycerol using $Fe_2O_3$ coated alumina catalyst [5] was also produced in order to examine the use of a product which would be highly characteristic of one produced in an industrial process.

### 2.3. Analysis of reaction mixture

The composition of the reaction mixture was monitored by extracting aliquots of reactant material (~0.03 g) through the septum with a syringe which was then analysed by gas chromatography. Quantification of species concentrations in the reaction mixture was primarily obtained using an Agilent HP 5890 gas chromatograph fitted with a Restek Stabilwax column and flame ionisation detector. Gas flows were carrier gas ($N_2$): 30 mL $min^{-1}$, $H_2$: 40 mL $min^{-1}$, air: 400 mL $min^{-1}$ and split ratio of 100:1. The injector temperature was 130 °C, detector temperature 270 °C and the temperature profile was to hold the oven at 35 °C for 5 min, ramping to 245 °C over 10 min and holding at 245 °C for 25 min. Identification of any unknown species was performed using an Agilent HP 6890 gas chromatograph fitted with a Restek CarboWax silica capillary column and 5973 mass-selective detector. Carrier gas used was helium, at a rate of 130 mL $min^{-1}$ with a split ratio of 5:1. The injector temperature was 130 °C, detector temperature was 235 °C and the temperature profile was to hold the oven at 35 °C for 5 min, ramping to 220 °C over 10 min and holding at 245 °C for 30 min. The MSD filament was turned off during elution of the solvent peak in order to protect the equipment. The data obtained from these instruments was then used to calculate the conversion and selectivity of reactant species. The fractional conversion of allyl alcohol, $X_{AA}$, and selectivity to glycidol, $S_{glc/AA}$ (mol percent) were calculated according to the following:

$$X_{AA} = \frac{[AA]_0 - [AA]_t}{[AA]_0} \tag{1}$$

$$S_{glc/AA} = \frac{[glc]_t \; MW_{AA}}{X_{AA}[AA]_0 \, MW_{glc}} \times 100 \tag{2}$$

where $[AA]$ is the concentration of allyl alcohol in the reaction mixture (ppm) at times corresponding to the subscripts 0 (initially) and $t$ (at the time specified) and $[glc]$ is the concentration of glycidol in the reaction mixture (ppm). $MW_{AA}$ and $MW_{glc}$ corresponds to the molecular mass of allyl alcohol (*AA*, 58.08 g $mol^{-1}$) and glycidol (*glc*, 74.08 g $mol^{-1}$), respectively. The selectivity of allyl alcohol to its associated by-products was obtained in the same way as for glycidol. In the case of by-products resulting from the oxidation of an impurity, the conversion of that impurity was first calculated as outlined in Eq. (1) and selectivity was calculated according to Eq. (2). Allyl alcohol or glycidol concentration in Eq. (1) and (2) were replaced with concentrations of impurity and oxidised impurity, respectively.

## 3. Results

### 3.1. Catalyst synthesis

The X-ray diffraction pattern (Fig. 2) shows that the zeolite synthesised is highly crystalline with a peak distribution corresponding to the MFI zeolite structure and an average crystallite size of ca. 62 nm. No significant quantity of amorphous material was detected as indicated by the absence of a broad absorption at approximately $2\Theta = 10^\circ – 20^\circ$.

### 3.2. Effect of solvent type

Ally alcohol was reacted with hydrogen peroxide at 60 °C using three different solvents; methanol, ethanol and ethyl acetate. The results shown in Table 1 indicate that the highest conversion and