



## Priority Communication

## Chemical looping epoxidation

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## ABSTRACT

Chemical looping epoxidation of ethylene was demonstrated, whereby the sole oxidant was a solid oxygen carrier, 15 wt% Ag supported on SrFeO<sub>3</sub>. Ethylene reacted with a bed of carrier particles, without any O<sub>2(g)</sub> in the feed, to produce ethylene oxide (EO) and CO<sub>2</sub>. Following the reduction by the C<sub>2</sub>H<sub>4</sub> of the SrFeO<sub>3</sub>, it was regenerated by passing air through the bed. The rate of reoxidation was slow, with full regeneration being achieved only by prolonged oxidation at elevated temperatures. A striking synergy between Ag and SrFeO<sub>3</sub> was observed solely when they were in intimate contact, suggesting a basis for a proposed reaction mechanism.

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## 1. Introduction

Ethylene oxide (EO) is an industrially-significant chemical intermediate, with a global production of 26 million tonnes in 2013 [1]. It is used in the synthesis of polymers, antifreeze, surfactants, solvents, etc. The predominant technology for its production is the epoxidation of ethylene with air or purified oxygen. Silver is the only catalyst used because no other material matches its performance [2].

A key intermediate species in the reaction mechanism is the oxygen adatom (O<sub>a</sub>), which is the selective oxygen species responsible for the epoxidation and, depending on its electrophilicity, combustion [3]. In the conventional process, where ethylene and gaseous oxygen are co-fed to the reactor, O<sub>a</sub> is generated from the dissociative adsorption of O<sub>2(g)</sub>. To date, there have been no reports of O<sub>a</sub> being directly supplied from a solid oxidant, probably because of the challenging requirements imposed on such a material. Working catalysts typically operate at partial pressures of O<sub>2</sub> of up to 2 bar and temperatures of 200–300 °C [2], where evidence suggest the existence of surface silver oxide phases [4–6]. Herein, it is therefore posited that the solid oxidant needs to have a high chemical potential of oxygen, μ<sub>O<sub>2</sub></sub>, to stabilise these active phases, or at least to ensure a sufficiently high surface coverage of O<sub>a</sub>. Such a high μ<sub>O<sub>2</sub></sub> at these temperatures is rare among solid oxides. Sufficiently fast ionic conduction is also required to replenish O<sub>a</sub> during the reaction, but oxide ion conduction is typically slow at these

temperatures. Lastly, the solid oxidant needs to be regenerable without significant loss of oxygen-storage capacity and kinetic activity.

A recent, large-scale *in silico* screening of materials has identified SrFeO<sub>3</sub> as a potential oxygen carrier for chemical looping combustion [7]. It was found that SrFeO<sub>3</sub> can release O<sub>2(g)</sub> reversibly over many cycles of thermal decomposition followed by reoxidation at low temperatures (~673 K, pO<sub>2</sub> = 0.15 bar), demonstrating its favourable μ<sub>O<sub>2</sub></sub> and kinetics. Crucially, SrFeO<sub>3</sub> does not react with CO<sub>2</sub> significantly [7] and thereby deactivate with the formation of carbonate, a problem afflicting other possible materials with a similar μ<sub>O<sub>2</sub></sub> such as SrO<sub>2</sub>/SrO and BaO<sub>2</sub>/BaO [8]. Resistance against carbonation is necessary because significant levels of CO<sub>2</sub> are generated from side reactions during epoxidation.

These favourable properties suggested the possibility of interfacing SrFeO<sub>3</sub> with Ag; SrFeO<sub>3</sub> could then supply oxygen to Ag as bulk or subsurface oxygen (O<sub>ss</sub>), where the oxygen could then diffuse to the silver surface to be presented as O<sub>a</sub> to effect the epoxidation in the absence of O<sub>2(g)</sub>. The concept is summarised in Fig. 1. The catalyst is then regenerated in air in a separate step to complete the chemical looping cycle.

It is advantageous to perform selective oxidations using a solid oxidant, in the absence of O<sub>2(g)</sub>, because this avoids flammable mixtures and renders a safer process. The conversion of ethylene is no longer limited by the supply of O<sub>2(g)</sub>, decreasing the need to recycle unreacted ethylene – industrial processes tend to operate with limited amounts of O<sub>2</sub> with ethylene in excess [2]. Furthermore, separation costs can be reduced by avoiding the need to separate N<sub>2</sub> (from purifying either O<sub>2</sub> or the products). Minimising

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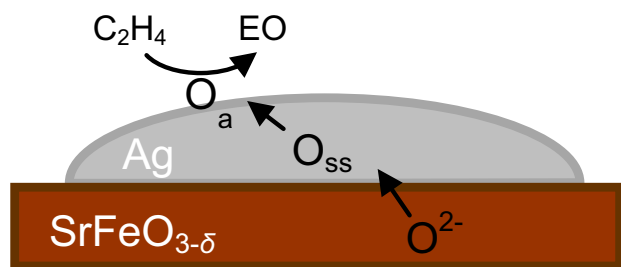


Fig. 1. Chemical looping epoxidation using a silver-modified oxygen carrier.

recycling, and combining unit operations of reaction and separation, are both examples of process intensification [9–11]. Lastly, improved selectivities may be achieved by the removal of  $O_{2(g)}$  [12].

In this work, we show that the epoxidation may be performed in the absence of  $O_{2(g)}$  by using a solid oxygen carrier. The aim is not to show competitive selectivities, so common promoters were not used (e.g. Cs and Cl), but rather to demonstrate the concept. We use the term ‘catalyst’ as an abbreviation for the ‘catalyst-oxygen carrier’ materials prepared in this study, where Ag acts as the catalyst and  $SrFeO_3$  acts as the oxygen carrier.

## 2. Experimental methods

$SrFeO_3$  was prepared by a solid-state synthesis method. Stoichiometric amounts of  $SrCO_3$  (0.72 mol) and  $Fe_2O_3$  (0.36 mol) were mixed in a ball mill for 3 h at 25 Hz. Ethanol (50 mL, 99.8%, Fisher Scientific) was added as a binder to improve mixing. The mixture was dried for 24 h at 50 °C, and sieved to 180–355  $\mu\text{m}$ . The particles were then calcined in four stages, with each stage consisting of calcination at 1000 °C for 3 h, followed by cooling to room temperature.

Incipient wetness impregnation was used to dose Ag onto supports, consisting of either  $SrFeO_3$  or  $\alpha\text{-Al}_2\text{O}_3$ . Prior to impregnation,  $SrFeO_3$  was sieved to a size range of 212 – 300  $\mu\text{m}$ , and  $\alpha\text{-Al}_2\text{O}_3$  (Alfa Aesar, product code 43862) was crushed and sieved to a size range of 212 – 300  $\mu\text{m}$ . The volume of solution added was equal to the pore volume of the support, which was determined empirically beforehand by adding deionised water dropwise with stirring to a mass of support. The endpoint was taken to be when the granular matter just started to cohere, i.e. when the internal pores have been filled and the mixture is at the onset of the pendular regime, when the volume of water added was taken to be equal to the pore volume. The pore volume of  $SrFeO_3$  was measured to be 0.24 mL/g, and the pore volume of  $\alpha\text{-Al}_2\text{O}_3$  was measured to be 0.26 mL/g. In a typical preparation of 15 wt% Ag/ $SrFeO_3$ , 1.3895 g of  $AgNO_3$  ( $\geq 99.0\%$ , Sigma-Aldrich) was dissolved in 1.2 mL water, which was then added dropwise to a batch of 5.0000 g  $SrFeO_3$  with agitation by a spatula. Correspondingly, in a typical preparation of 15 wt% Ag/ $\alpha\text{-Al}_2\text{O}_3$ , 1.3895 g of  $AgNO_3$  ( $\geq 99.0\%$ , Sigma-Aldrich) was dissolved in 1.3 mL water, which was then added dropwise to a batch of 5.0000 g  $\alpha\text{-Al}_2\text{O}_3$  with agitation by a spatula. The impregnated solids were then dried at 120 °C for 12 h in static air, before calcination at 500 °C for 5 h with a ramp rate of 5 °C/min in static air.

A packed bed reactor was used to perform the epoxidation experiments, and was operated in either chemical looping mode or co-feeding mode. The reactor consisted of an 8 mm i.d., 200 mm long quartz tube mounted vertically with a sintered disc fixed 75 mm from the bottom. The tube was wrapped with a high temperature dual-element heating tape (Omega, DHT052020LD). The output of the heating tape was controlled by a type K thermocouple with a mineral-insulated Inconel sheath inserted into the bed.

The bed was packed above the sintered disc, with a bottom layer of  $\alpha\text{-Al}_2\text{O}_3$  (Boud Minerals, 425–710  $\mu\text{m}$ ) to position the active bed in the isothermal region of the reactor, then a middle layer with the catalyst, then finally another layer of 3 g of  $\alpha\text{-Al}_2\text{O}_3$  to distribute and preheat the feed. Both ends of the quartz tube were connected to Swagelok Ultra-Torr® vacuum fittings and sealed with fluorocarbon FKM O-rings. A 7  $\mu\text{m}$  filter (Swagelok, SS-2TF-7) was fitted at the outlet of the reactor. *Ex situ* regeneration of the active material was performed by dismounting the reactor tube, containing the packed bed, from its fittings and placing it in a box furnace to be calcined at 400 °C for 2 h in static air.

The feed gases to the reactor were supplied from cylinders (BOC), and consisted of 5.16 vol%  $C_2H_4$  in balance  $N_2$  (certified to 5% uncertainty, BOC),  $N_2$  (purity  $> 99.998\%$ ), and bottled purified air. Gas flows were manipulated by calibrated rotameters and checked using a bubble film flowmeter at the start of each experiment. Gases were switched using digitally-controlled solenoid valves. Continuous online analysis of the gaseous products was achieved by a Fourier transform infrared (FTIR) analyser (MKS Instruments, Multigas 2030) equipped with a liquid  $N_2$ -cooled mercury-cadmium-telluride detector. Measurements were collected 2.5 h after filling the liquid  $N_2$  dewar, once the background has settled. The 5.11 m gas cell was heated to 150 °C. Each measurement consists of 8 scans of the band 800 – 4600  $\text{cm}^{-1}$ , lasting 1.87 s, at a resolution of 0.5  $\text{cm}^{-1}$ . The collected spectra were analysed for  $C_2H_4$ ,  $CO_2$ , ethylene oxide, CO and  $H_2O$ , using software (MKS, MG2000). The analysis regions for each quantified species were adjusted to exclude interfering peaks from other species to eliminate any cross-sensitivities. Negligible amounts of CO were detected,  $< 40$  ppm.  $H_2O$  was not quantified; its quantity was inferred from the stoichiometry of combustion,  $C_2H_4 + 3/2O_2 \rightarrow CO_2 + H_2O$ , i.e. 1 mol of  $CO_2$  generated implied that 1 mol of  $H_2O$  was also generated, and that 3 mol of O was consumed. No acetaldehyde was detected.

In the chemical looping experiments, the reactor was packed with 1.0 g  $\alpha\text{-Al}_2\text{O}_3$  for the bottom layer, with 2.000 g catalyst in the middle layer. A constant flow rate of 200 mL/min (measured at 293 K, 1 atm), was maintained at all times. The feed gases were switched automatically, with the base case cycling times of (i) reduction with 5.16 vol%  $C_2H_4$  in balance  $N_2$  for  $t_{red} = 1.5$  min, (ii) purge with  $N_2$  for 2 min, (iii) oxidation with compressed air for  $t_{ox} = 15$  min, and (iv) purge with  $N_2$  for 2 min.

The overall carbon balance in a particular reduction stage was calculated according to (assuming dilute gases and small conversions so that the total molar flow rate in and out of the reactor is constant)

$$\text{Carbon balance} = \frac{\text{Total carbon detected}}{\text{Total carbon fed}} = \frac{\int_{t_{start}}^{t_{end}} (y_{C_2H_4} + y_{EO} + \frac{1}{2}y_{CO_2} + \frac{1}{2}y_{CO}) dt}{y_{C_2H_4, feed} \cdot t_{red}} \quad (1)$$

where  $y_i$  is the mole fraction of species  $i$ ,  $t$  is time, and  $y_{C_2H_4, feed}$  is the mole fraction of  $C_2H_4$  in the feed. The start and end time for integration was the first and final points in time where EO was detected (the range of this time was not necessarily equal to  $t_{red}$  because of the response of the analyser). The carbon balance was always within  $95 \pm 5\%$ , and usually within  $98 \pm 5\%$ , which verifies that the rate of accumulation of coke in the reactor is small and may be neglected in subsequent analyses.

The cumulative amount of oxygen released by time  $t$ , in a particular cycle starting at time  $t_{start}$ , was calculated by integrating all the oxygenated gaseous products according to

$$\text{Mol O released}(t) = F \int_{t_{start}}^t (y_{EO} + 3y_{CO_2} + y_{CO}) dt \quad (2)$$

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